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Solar energy storage using phase change materials ☆

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Abstract

The continuous increase in the level of greenhouse gas emissions and the climb in fuel prices are the main driving forces behind efforts to more effectively utilise various sources of renewable energy. In many parts of the world, direct solar radiation is considered to be one of the most prospective sources of energy. However, the large-scale utilisation of this form of energy is possible only if the effective technology for its storage can be developed with acceptable capital and running costs. One of prospective techniques of storing solar energy is the application of phase change materials (PCMs). Unfortunately, prior to the large-scale practical application of this technology, it is necessary to resolve numerous problems at the research and development stage. This paper looks at the current state of research in this particular field, with the main focus being on the assessment of the thermal properties of various PCMs, methods of heat transfer enhancement and design configurations of heat storage facilities to be used as a part of solar passive and active space heating systems, greenhouses and solar cooking.

Keywords: Phase change materials (PCMs); Latent heat storage; Solar greenhouses; Solar cookers; Heat transfer

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Contents

1. Introduction

Fundamental investigations of effective methods of thermal energy storage have been significantly intensified since the 1973–1974 energy crisis, with numerous countries commencing development programs of power systems utilising non-conventional energy sources at both the national and international level. The results obtained from these investigations have been published in many research papers and academic books, see for example monographs by Schaetzle [1], Schmidt [2], Beckmann and Gill [3], Garg et al. [4] and Garg [5]. General principles and various technologies for solar energy storage were summarised by Garg et al. [4]. A great number of scientific publications and patents on latent heat storage for solar energy conservation stimulated the appearance of Lane's monograph [6,7], with a review of the information on this subject which was available at the time of publication. Another monograph dedicated to the problems of thermal energy storage was prepared by Dincer and Rosen [8].

In [9], the following phase change material (PCM) properties to be used for latent heat storage were highlighted as desirable:

1. a high value of the heat of fusion and specific heat per unit volume and weight,
2. a melting point which matches the application,
3. a low vapour pressure (<1 bar) at the operational temperature,
4. a chemical stability and non-corrosiveness,
5. a PCM should not be hazardous, highly inflammable or poisonous,
6. a PCM should have a reproducible crystallisation without degradation,
7. a PCM should have a small supercooling degree and high rate of crystal growth,
8. a PCM should have a small volume variation during solidification,
9. a high thermal conductivity,
10. a PCM should be of abundant supply and at a low cost.

Some natural substances, such as salt hydrates, paraffin and paraffin waxes, fatty acids and other compounds, have the required high latent heat of fusion in the temperature range from 0 to 150 °C and these materials could be used for solar applications, though have certain shortcomings. The main limitation of salt hydrates is their chemical instability when they are heated, as at elevated temperatures they degrade, losing some water content every heating cycle. Furthermore, some salts are chemically aggressive towards structural materials and they have a low heat conductivity. Finally, salt hydrates have a relatively high degree of supercooling.

The natural paraffins are a mixture of pure alkanes which have quite a wide range of the phase change temperature. These paraffins also have a low heat conductivity and therefore the choice of those which can be used for practical solar applications is very limited.

The common shortcoming of many potential phase change heat storage materials is their low heat conductivity. This is between 0.15 and 0.3 W/(mK) for organic materials and between 0.4 and 0.7 W/(mK) for salt hydrates. The operational temperature range for low-temperature solar units and devices is in the interval between 20 and 80 °C. In these conditions, the intensity of heat transfer processes is very sensitive to the temperature gradient between heat carriers.

Methods to minimise the negative effect of the shortcomings listed above were considered by Lane [6,7]. However, there is an ongoing search for new techniques and means to resolve this problem. In [10], the properties of more than one hundred organic and inorganic materials and compositions were analysed for a potential application in solar thermal storage systems. Additionally, some methods of preventing or decreasing the level of supercooling of salt hydrates were described and the factors affecting their stability and maintaining their high heat storage capability were considered. Compositions on the basis of calcium chloride hexahydrate, sodium sulphate decahydrate (Glauber's salt) and sodium acetate trihydrate were analysed in more details and problems of the chemical compatibility of PCMs and structure materials were addressed.

Hasnain [11,12] published results of a comparison of sensible and latent heat properties of different materials which could be used in solar thermal storages. Thermo-physical properties of some salt hydrates and organic materials have been compiled. It was pointed out that, while the technology of the thermal storage using a sensible heat property was at the mature stage and broadly applied, the large-scale use of PCMs would require a thorough study of their thermo-physical properties in solid and liquid states. Technologies for cold storage were also considered and the experience gained in USA and Canada summarised, with a conclusion made that cold storage technologies could be successfully used for air conditioning in countries with hot climate.

Recent advances in the field of the cold storage were also reviewed by Saito [13]. The author analysed results from 137 publications in this field. Characteristics of commercial systems and methods of modelling and control were analysed. Furthermore, technical problems of ice production, accumulation, transportation and application of the accumulated ice were highlighted.

Results of a critical review of 237 sources in the area of thermal energy storage using PCMs were presented by Zalba et al. [14]. In this work, the main attention also was on thermo-physical properties of PCMs which could be used in solar applications. One of the conclusions made was that PCM thermo-physical properties had not been

studied sufficiently in order that clear recommendations could be made for a design process of commercial heat storage units (HSUs). It should be noted that even now there is no comprehensive database on thermo-physical properties available. This information must be obtained by applying established rigorous thermo-physical methods, which are usually used as the basis for investigations of other matters in solid and liquid states over wide temperature ranges. This state can be partially explained by the chemical instability of pure salt hydrates, which makes it difficult to maintain a stoichiometric composition during tests. Another obstacle is that these thorough measurements of properties are quite expensive to perform. Authors point out the existence of large discrepancies in data for the melting temperature and latent heat for the same PCMs. A part of [14] is dedicated to the assessment of analysis of the heat transfer which takes place during melting and solidification processes. There are numerous research activities which are aimed to resolve this task theoretically for simplified cases. At the same time, there is a deficit of available experimental data which can be used for the calibration of developed theoretical models. Finally, the authors highlighted areas where heat storage devices have been used, see Table 1. As it can be seen from the table, the thermal storage of solar energy can be considered as one of prospective applications for PCMs.

The analysis of properties of PCMs and possibilities of application in the form of a hermetic encapsulation were the focus in [15]. Authors emphasised existing problems of separation, supercooling and stability of thermal properties in the long-time cycle processes. Difficulties accompanying the hermetic micro- and macro-encapsulation and methods of heat transfer enhancement were also briefly addressed in this work.

Finally, Mehling and Hiebler [16], in the framework of the special International Energy Agency Programme, summarised results of the most recent investigations on the application of PCMs in buildings. Many of the PCMs considered in this review were in the developmental and trial phase and therefore some essential data on their properties was unavailable. The authors present information on several PCMs on the basis of salt hydrates and paraffins, which are commercially produced by Rubitherm GmbH and Climator AB. The work also looks at the advantages and shortcomings of different ways of cold storage in buildings.

Table 1
Application of PCMs in thermal energy storage systems

Cooling of heat and electrical engines
Cooling: use of off-peak rates
Cooling: food, wine, milk products (absorbing peaks in demand), greenhouses
Heating and hot water: using off-peak rates
Medical applications: transportation of blood, operating tables, hot–cold therapies
Passive storage in bio-climatic building/architecture (HDPE, paraffin)
Safety: temperature level maintenance in rooms with computers or electrical/electronic appliances
Smoothing exothermic temperature peaks in chemical reactions
Solar power plants
Spacecraft thermal systems
Thermal comfort in vehicles
Thermal protection of electronic devices (integrated in the appliance)
Thermal protection of food: transport, hotel trade, ice-cream, etc.
Thermal storage of solar energy

Analysis of the above publications dedicated to PCMs show that there are some uncertainties when considering PCMs for the solar energy application:

- It is not clear to what extent thermo-physical properties of PCMs were investigated and how reliable any data is.
- Since there is considerable discrepancy in the data provided on thermo-physical properties of commercially available PCMs, then it is not obvious whether this data is verified by independent research institutions using established classical testing methods.
- There is no commonly accepted criteria on the magnitude of heat conductivity of commercially available PCMs to decide whether a PCM could be used for solar applications.
- It is not clear whether the heat and mass transfer process investigations were performed for a commercially available PCM so that results obtained could be used in designing the solar energy device.
- It is difficult to determine whether it is feasible to use a certain PCM for a solar energy application even if there is information on its cost.
- In what directions the research should be pursued in order to promote application of PCMs for solar energy storage?

The present work analyses the publications over the last 15 years on the properties and the applications of PCMs and methods of enhancing heat and mass transfer in storage devices.

2. Recent investigations on PCMs

2.1. Organic materials

Among organic materials, fatty acids mostly attract the attention of specialists. These are relatively cheap and therefore are widely used in different areas. The range of the melting temperature of fatty acids varies from −5 to 71 °C, while the latent heat of fusion varies from 45 to 210 kJ/kg. Data from investigations of some fatty acids is presented in Table 2. It can be seen that the measured heat of fusion for different fatty acids varies over a very wide range. Thus, for lauric acid it is between 176 and 211 kJ/kg, for myristic acid from 175 to 205 kJ/kg, for palmitic acid between 189 and 203 kJ/kg and, finally, for stearic acid from 159 to 211 kJ/kg. All the values of the heat of fusion and specific heat were measured with the use of the differential scanning calorimetry (DSC) method.

Table 3 presents data on the properties of fatty acid compositions which can be used for solar energy storage.

The chemical compounds and eutectic compositions are less attractive from the application point of view than the mixtures of commercially manufactured fatty acid products. Therefore, Feldman et al. [38–40] investigated the properties of various compositions on the basis of fatty acids produced by Henkel, Canada. Some fatty eutectics have quite strong odour and therefore they are not recommended for use as wallboard PCMs.

The properties of some *n*-alkanes and their mixtures are presented in Tables 4 and 5.

As in the case with fatty acids, one can see significant discrepancies in the measured heat of fusion for pure *n*-alkanes. For example, the heat of fusion value for dodecane varies

Table 2
Thermo-physical properties of some of investigated fatty acids

Heat storage material	Manufacturers of fatty acids	Purity of fatty acids	Melting point (°C)	Heat of fusion (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Heat conductivity (W/mK)	Density solid/ liquid (kg/m^3)	References
Capric acid	Fluka Chemie AG		30.1	158				Kauranen et al. [17] Peippo et al. [18]
			30.1	150–158	1.95/1.60–1.72	0.16 (s)		Zhang et al. [19]
	Tokyo Chemical, Inc.	98 wt%	31.4	150.6				Dimaano and Watanabe [20]
Lauric acid	Tokyo Chemical, Inc.	98 wt%	43.7	210.8				Dimaano and Watanabe [20]
	Not available		42.44	185.5				Zhang et al. [21]
	Not available	95 wt%	41–43	211.6	1.76 (25 °C)/ 2.27 (°C)	0.16 (s)	1007/862	Sarı and Kaygusuz [22]
	Fluka Chemie AG		41.3	179				Kauranen et al. [17] Peippo et al. [18]
			52.1–52.5	160–179	1.60–1.17 (l)	0.15–0.17 (s)		Zhang et al. [19]
	Fluka Chemie AG	97 wt%	42.6	211.6	1.7/2.3			Sarı [23]
	Fluka Chemie AG	97 wt%	42.6	176.6				Sarı and Kaygusuz [24]
	Not available			186 ± 10	2.81 ± 0.60/ 2.14 ± 0.46			Hong et al. [25]
Myristic acid			50.4–53.6	189				Hasan and Sayigh [26]
			49.7–52.7	190–201	2.91/3.67	0.17 (s)		Zhang et al. [19]
	Not available	Chemical	52.7	175.7				Dotsenko et al. [27]
	Merck	98 wt%	51.5	204.5	2.8 (35 °C)/2.42 (70 °C)			Sarı and Kaygusuz [28]
	Fluka Chemie AG		52.1	190				Kauranen et al. [17] Peippo et al. [18]
	Fluka Chemie AG	95 wt%	53.8	192.0	1.7/2.4			Sarı [23]
	Aldrich	95 wt%	53.0	181.0				Sarı and Kaygusuz [24]

Pentadecane acid			52.5	158.6		Dotsenko et al. [27]
Palmitic acid			57.8–61.8	201		Hasan and Sayigh [26]
	Not available		63.28	202.9		Zhang et al. [21]
	Merck	99.3 wt%	64.0	208.2		Cedeno et al. [29]
	Merck	97 wt%	61.0	203.4	2.20 (40 °C)/ 2.48 (80 °C)	Sarı and Kaygusuz [30]
	Fluka Chemie AG		54.1	183		Kauranen et al. [17] Peippo et al. [19]
	Fluka Chemie AG	95 wt%	59.9	197.9	1.9/2.8	Sarı and Kaygusuz [28]
	Merck	90 wt%	61.3	197.9		Sarı [23]
	Not available	Chemical	63.5	188.7		Dotsenko et al. [27]
Stearic acid			65.2–68.5	210		Hasan and Sayigh [26]
	Not available	Chemical	69.6	176.2		Dotsenko et al. [27]
		Com. grad	66	155		Sharma et al. [31,32]
	Fluka Chemie AG		64.5	196		Kauranen et al. [17] Peippo et al. [18]
	Merck	97 wt%	71.0	210.8		Cedeno et al. [29]
	Merck	90 wt%	60–61	186.5	2.83 (40 °C)/ 2.38 (80 °C)	Sarı [33]
	Merck	90 wt%	54.7	159.3		Sarı [23]
Oleic acid	Merck	99.9 wt%	−5.3	75.5		Cedeno et al. [29]
	ED and L Industries, Inc.	90 wt%		45.3		Dimaano and Watanabe [20]

Table 3
Thermo-physical properties of some acid compositions and alkyl esters

Heat storage composition	Type of composition	Melting point (°C)	Heat of fusion (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Heat conductivity (W/mK)	References
Carpic acid (655 mol%) + lauric acid (35 mol.%)	Eutectic	18–19.5	140.8	1.97/2.24	0.143/0.139	Dimaano and Watanabe [20]
Carpic acid (61.5 wt%) + lauric acid (38.5 wt%)	Eutectic	19.1	132			Kauranen et al. [17]; Peippo et al. [18]
Carpic acid + Lauric acid	Eutectic	18	120			Feldman et al. [34]
Carpic acid (73.5 wt%) + myristic acid (26.5 wt%)	Eutectic	21.4	152			Kauranen et al. [17]; Peippo et al. [18]
Carpic acid (75.2 wt%) + palmitic acid (24.8 wt%)	Eutectic	22.1	153			Kauranen et al. [17]; Peippo et al. [18]
Carpic acid (86.6 wt%) + stearic acid (13.4 wt%)	Eutectic	26.8	160			Kauranen et al. [17]; Peippo et al. [18]
Lauric acid (62.6 wt%) + myristic acid (37.4 wt%)	Eutectic	32.6	156			Kauranen et al. [17]; Peippo et al. [18]
Lauric acid (66.0 wt%) + myristic acid (34.0 wt%)	Eutectic	34.2	166.8			Sarı [33]
Lauric acid (64.0 wt%) + palmitic acid (36.0 wt%)	Eutectic	32.8	165			Kauranen et al. [17]; Peippo et al. [18]
Lauric acid (69.0 wt%) + palmitic acid (31.0 wt%)	Eutectic	35.2	166.3			Sarı [33]; Tunçbilek et al. [35]
Lauric acid (77.0 wt%) + palmitic acid (23.0 wt%)	Eutectic	33.0	150.6	1.77/2.41		Zhang et al. [21]
Lauric acid (80.0 wt%) + palmitic acid (20.0 wt%)	Eutectic	32.7	145			Feldman et al. [34]
Lauric acid (75.5 wt%) + stearic acid (24.5 wt%)	Eutectic	37.3	171			Kauranen et al. [17]; Peippo et al. [18]
Lauric acid + stearic acid	Eutectic	34	150			Feldman et al. [34]
Lauric acid (75.5 wt%) + stearic acid (24.5 wt%)	Eutectic	37	182.7	1.92/2.10		Sarı and Kaygusuz [36]
Myristic acid (51 wt%) + Palmitic acid (49 wt%)	Eutectic	39.8	174			Kauranen et al. [17]; Peippo et al. [18]
Myristic acid (58 wt%) + palmitic acid (42 wt%)	Eutectic	42.6	169.7			Sarı [23]

Myristic acid (65.7 wt%) + stearic acid (34.7 wt%)	Eutectic	44	181	Kauranen et al. [17]; Peippo et al. [18]
Myristic acid (64.0 wt%) + stearic acid (36.0 wt%)	Eutectic	44	182	Sarı [33]
MA_3PA_2 (myristic acid + palmitic acid)	CC[a]	47.3	173.8	Dotsenko et al. [27]
MA_2SA (myristic acid + stearic acid)	CC	48.6	179.8	Dotsenko et al. [27]
Palmitic acid (64.9 wt%) + stearic acid (35.1 wt%)	Eutectic	50.4	181	Kauranen et al. [17]; Peippo et al. [18]
Palmitic acid (64.2 wt%) + stearic acid (35.8 wt%)	Eutectic	52.3	181.7	Baran and Sarı [37]
Palmitic acid + stearic acid	Eutectic	51	160	Feldman et al. [34]
Palmitic acid (50 wt%) + stearic acid (45.5 wt%) + other fatty acids (4.5 wt%)—*emersol 132*	Mixture	54–57	180	Feldman et al. [38]
PeASA (pentadecane acid + stearic acid)	CC	50.6	173.0	Dotsenko et al. [27]
Stearic acid (65 wt%) + palmitic acid (27.5 wt%) + other fatty acids (5.5 wt%)—*emery 420*	Mixture	51–56	180	Feldman et al. [38]
PASA (palmitic acid + stearic acid)	CC	57.2	179.6	Dotsenko et al. [27]
Stearic acid (83 wt%) + palmitic acid (11 wt%) + other fatty acids (6% wt%)—*emersol 150*	Mixture	60–66	206	Feldman et al. [38]
Stearic acid (95 wt%) + palmitic acid (5 wt%)—*emersol 153*	Mixture	65–68	209	Feldman et al. [38]
Butyl palmiate (49 wt%) + butyl stearate (48 wt%) + other (3 wt%)	Mixture	17	140	Feldman and Banu [39]
Methyl palmiate (65–90 wt%) + methyl stearate (35–10 wt%)	Mixture	22–25.5	120	Feldman et al. [40]
Methyl stearate	CC	29.0	169	Suppes et al. [41]
Methyl palmitate	CC	38.0	180	Suppes et al. [41]
Ethyl stearate	CC		134	Suppes et al. [41]
Ethyl palmitate	CC	23.0	122	Suppes et al. [41]

[a]CC—chemical compound.

Table 4
Thermo-physical properties of some pure *n*-alkanes

n-alkane	Transition temperature (°C)	Heat of transition (kJ/kg)	Melting point (°C)	Heat of fusion (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Density solid/liquid (kg/l)	References
Dodecane				135±8	5.11±0.56/ 2.19±0.19		Hong et al. [25]
			−9.6	216	2.21 (80 °C)		Himran et al. [42]
Tetradecane			5.9	258		0.77 (liq.)	Dotsenko et al. [27]
			5.8	227	2.22 (liq.)	0. 759 (20 °C)	Himran et al. [42]
Purity—99%			5.4	227.5			He et al. [43]
Purity—99%			3.64	172.1			Cho and Choi [44]
Pentadecane	−2	64.12	9.9	193.9		0.765 (20 °C)	Dotsenko et al. [25]
			9.9	207	2.22 (liq.)		Himran et al. [42]
			9.9	206			He et al. [43]
Hexadecane			18.1	236	2.22 (liq.)	0.770 (20 °C)	Himran et al. [42]
			17.9	211.5			He et al. [43]
				225±15.2	2.25±0.25/ 2.20±0.11		Marin et al. [45]
Industrial grade			13.2–13.9	201			Nagano et al. [46]
Heptadecane			20.8–21.7	171–172	2.57 (s)		Zhang et al. [19]
Octadecane			28	250.7			Dotsenko et al. [27]
			28.1	244	1.91/2.22	0.779 (20 °C)	Himran et al. [42]
Industrial grade			24.7–28.2	203			Nagano et al. [46]
Heneicosane	32.8	80.94	40	155.49			Dotsenko et al. [27]
			40.2	213		0.778 (20 °C)	Himran et al. [42]
Docosane			44	196.4			Dotsenko et al. [27]
			44	252			Himran et al. [42]
			54.6–57.7	216–237	3.89/2.94		Zhang et al. [19]

from 135 to 216 kJ/kg, for tetradecane from 172 to 258 kJ/kg, for octadecane from 203 to 251 kJ/kg, etc. While studying some chemically pure organic matters, Dotsenko et al. [27] found that *n*-alkanes with odd numbers of carbon atoms in the molecule, such as pentadecane and heneicosane, have phase transition in their solid state. Since dodecane does not have this phase transition in its solid state, then its specific heat of 5.11 kJ/kgK, registered by Hong et al. [25] might be inaccurate (this value is much greater than the same property of water). Consequently, the heat of fusion for dodecane reported in [25] also needs careful consideration. It should be noted that the above substances are quite expensive and their application is restricted to special heat storage systems only. Commercial paraffins and paraffin waxes are more attractive for application in solar heating systems since these materials are produced in large quantities and widely used elsewhere. The information on thermo-physical properties of some paraffins and paraffin waxes is presented in Table 6.

While studying sugar alcohol as a PCM, Kakuichi et al. [51] found that the properties of erythritol are such that it can be successfully used as a heat storage material, see Table 7. Its latent heat of fusion was measured by using a Seiko differential scanning calorimeter

Table 5
Thermo-physical properties of some eutectic composition of *n*-alkanes

Heat storage composition	Type of composition	Transition temperature (°C)	Heat of transition (kJ/kg)	Melting point (°C)	Heat of fusion (J/kg)	Sensible heat solid/ liquid (kJ/kg °C)	Heat conductivity (W/mK)	Density solid/ liquid (kg/l)	References
Tetradecane (91.67 mole.%) + hexadecane (8.33 mole.%)	Eutectic			1.7	156.2				He et al. [43]
Tetradecane + geneicosane	Eutectic			3.54–5.56	200.28				Dotsenko et al. [27]
Tetradecane + octadecane	Eutectic			(−4.02)–2.1	227.52				Dotsenko et al. [27]
Tetradecane + docosane	Eutectic			1.5–5.6	234.33				Dotsenko et al. [27]
Pentadecane + heneicosane	Eutectic	1.69	48.10	6.23–7.21	128.25				Dotsenko et al. [27]
Pentadecane + octadecane	Eutectic	2.16	68.81	8.5–9.0	271.93				Baran and Sarı [37]
Pentadecane + docosane	Eutectic	−2.88	83.37	7.6–8.99	214.83				Dotsenko et al. [27]
Octadecane + heneicosane	Eutectic	−3.0	26.60	25.8–26.0	173.93				Dotsenko et al. [27]
Octadecane + docosane	Eutectic			25.5–27.0	203.8				Dotsenko et al. [27]

Table 6
Thermo-physical properties of some commercial paraffins and paraffin waxes

Heat storage material	Transition temperature (°C)	Melting range (°C)	Heat of fusion including transition heat (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Heat conductivity (W/mK)	Density solid/ liquid (kg/l)	References
Suntech P116 Parrafin wax		43–56	266	2.95/2.51	0.24/0.24	0.818/0.760	Himran et al. [42]
Unicere 55 Paraffin		52.5–53.7	182–189				Lee et al. [47]
Paraffin 44		44	167				Farid et al. [48]
Parraffin 53		53	200				Farid et al. [48]
Paraffin 64		64	210				Farid et al. [48]
Paraffin 56 (Russia)		56±2	72–86		0.75 (25 °C)	1.06	Dotsenko et al. [27]
Paraffin 57 (Russia)		57±2	98		0.7		Dotsenko et al. [27]
Paraffin 63 (Russia)		63±2	60				Dotsenko et al. [27]
Paraffin natural wax 79 (Russia)		79±2	80		0.63	1.20	Dotsenko et al. [27]
Paraffin natural wax 84 (Russia)		84±2	85		0.72	1.20	Dotsenko et al. [27]
Paraffin natural wax 106 (Russia)		106±2	80		0.65	1.20	Dotsenko et al. [27]
Paraffin wax 53 (commercial grade)		53	184	2.05			Sharma et al. [31,32]
Paraffin 53	35.4	53	164	2.13 (30 °C)/ 2.62 (70 °C)	0.28 (30 °C)/ 0.19 (70 °C)	0.978 (30 °C)/ 0.795 (70 °C)	Inaba and Tu [49]
RT 60 Rubitherm paraffin		58–60	214	0.93	0.2	0.850/0.775	Velraj et al. [50]

Table 7
Melting point, heat of fusion and cost of typical sugar alcohol (Kakiuchi et al. [51])

Material	Melting point (°C)	Heat of fusion (kJ/kg)	Density (kg/l) (at 20 °C)	Cost (US$/kg)
Erythritol	120	339.8	1.45	5.0
D-mannitol	166–168	316.4	1.52	6.7–7.5
Galactitol	188–189	351.8	1.47	—
Xylitol	93–94.5	263.3	1.52	6.7–8.3
D-sorbitol	96.7–97.7	185.0	1.50	1.1

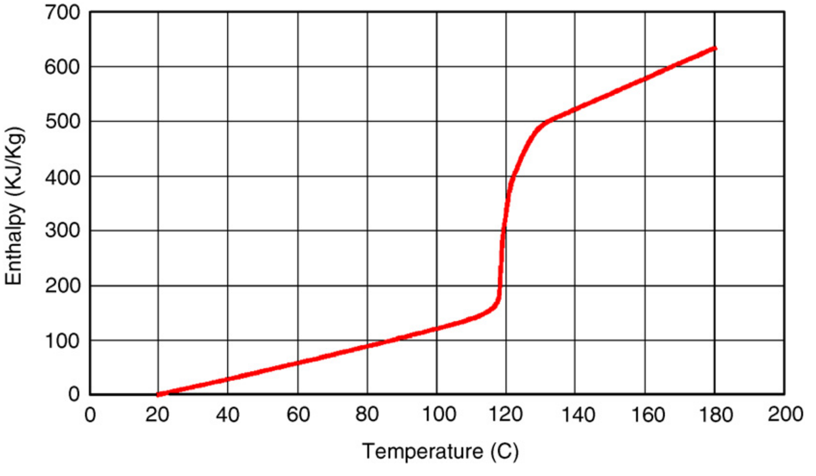


Fig. 1. The variation of enthalpy of erythritol [51].

and its specific heat was determined using an adiabatic calorimeter. The variation of enthalpy, obtained from the tests, is shown in Fig. 1. The thermo-physical properties of the investigated samples of erythritol are presented in Table 8. It can be seen that erythritol behaves similar to ice and melts congruently. Its heat of fusion is 320 kJ/kg which is almost equal to that for ice. A specific feature is its high-density value. It should be noted that there is also a 10% change in erythritol's volume during the solid-to-liquid transition and therefore the storage vessel and heat exchanges need to be designed to take this into account. A supercooling phenomenon was observed during the experimental investigations. It was found that the freezing range for this material is 60–100 °C. Shukla et al. [54], when performing accelerated thermal cycle tests of erythritol, found that samples of commercial erythritol showed no signs of degradation during 75 thermal cycles and reported that the erythritol was supercooled by 15 °C.

Finally, mixtures on the basis of trimethylethane hydrate (TME), produced by Wako Pure Chemical Industries, were proposed by Kakuichi et al. [56] for use as a heat storage material, with their thermal properties also determined using a Seiko differential scanner calorimeter.

2.2. Inorganic materials

The inorganic materials have not been investigated as heat storage materials to the same extent as the organic ones have. Prospective heat storage materials, such as salt hydrates,

Table 8
Thermo-physical properties of some organic and inorganic materials

Heat storage composition	Type of composition	Melting point (°C)	Heat of fusion (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Heat conductivity (W/mK)	Density solid/liquid (kg/l)	References
Acetamide (commercial grade)	Chemical compound	82	263	1.94		1.159/0.998	Sharma et al. [32,52]
Acetanilide (commercial grade)	Chemical compound	118.9	222	2.00			Buddhi et al. [53]
Erythrol (food additive grade)	Chemical compound	118	339.8	1.38 (20 °C)/2.76 (140 °C)	2.64 (20 °C)/1.17 (140 °C)	1.48 (20 °C)/1.30 (140 °C)	Kakuichi et al. [51]
Erythritol (commercial grade of Mitsubishi Chemical Co.)		116 ± 2	338 ± 7				Shukla et al. [54]
Trimethylolethane (62.5 wt%) + water (37 wt%)—(PCM30)	Mixture	29.8	218	2.75 (10 °C)/3.58 (50 °C)	0.65 (22 °C)/0.21 (56 °C)	1.12 (10 °C)/1.09 (56 °C)	Kakuichi et al. [56]
Trimethylolethane (38.5 wt%) + water (31.5 wt%) + urea (30 wt%)—(PCM13)	Mixture	14.4	160	4.22 (0 °C)/3.09 (30 °C)	0.66 (5 °C) /0.37 (38 °C)	1.17 (0 °C)/1.14 (30 °C)	Kakuichi et al. [56]
$Mn(NO_3)_2 \cdot 6H_2O + MnCl_2 \cdot 4H_2O$ (4.0 wt%)	Mixture	15–25	125.9	2.34 (4.4 °C) 2.78 (13.7 °C)		1.795 (5 °C)/1.728 (40 °C)	Nagano et al. [57,46]
$Mg(NO_3)_2 \cdot 6H_2O$	Chemical compound	89.3–89.9	167–175	1.84/2.51	0.57 (120 °C)		Zhang et al. [19]
$Mg(NO_3)_2 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$ (7.0 wt%)	Mixture	77.2–77.9	150.7–152.4	3.72 (50 °C)			Nagano et al. [58]
$Mg(NO_3)_2 \cdot 6H_2O$ (58.7 wt%) + $MgCl_2 \cdot 6H_2O$ (41.3 wt%)	Mixture	58.0–58.3	120–132	1.94/2.57	0.61–0.68 (s)		Zhang et al. [19]
$Mg(NO_3)_2 \cdot 6H_2O$ (62.5 wt%) + NH_4NO_3 (37.5.3 wt%)	Mixture	48.7–51.0	118–126	2.60/2.56	0.34 (s)		Zhang et al. [19]
$NaCH_3COO \cdot 3H_2O$	Hydrated salt	58	267	2.79/4.57	0.63 (solid)	1.45/1.28	Freitag [59]
			245 ± 9	2.26 ± 0.13/3.74 ± 0.59			Hong et al. [25]
		58.0	226–248	2.26–2.79/3.33	0.68 (s)		Zhang et al. [19]
$Na_2S_2O_3 \cdot 5H_2O$	Hydrated salt	48.0	201–206	3.83 (l)			Zhang et al. [19]

have disadvantages due to their instability, following dehydration in the process of thermal cycling and a high degree of supercooling. Therefore, the development of new salt compositions requires careful research and much longer time. Nagano et al. [46,57] discovered that manganese nitrate hexahydrate could be used as the basis for the development of a new heat storage composition. The melting range for this material varies from 7.7 to 25.3 °C and its heat of fusion is 125.9 kJ/kg. It was observed that salt has a significant degree of supercooling. They also examined the influence of introducing various additives to change the melting temperature, the heat of fusion and the degree of supercooling. For example, they discovered that adding manganese chloride tetrahydrate into $Mn(NO_3)_2 \cdot 6H_2O$ in quantities of up to 10% in weight did not change the heat of fusion value. They proposed to use the mixture with the following composition: $Mn(NO_3)_2 \cdot 6H_2O + 4.0\%$ in weight of $MnCl_2 \cdot 4H_2O$. The thermo-physical properties of such a composition are presented in Table 8. It was estimated that the cost of a commercial composition would be approximately 2 US$/kg which makes this substance competitive with organic PCMs to be used in the same temperature range.

The same researchers developed a different heat storage material on the basis of magnesium nitrate hexahydrate [58]. It is obvious that in order to be applied in large-scale practical storage systems, PCMs should have a purity grade of that of typical industrial products. In [58], the authors compared properties of reagent- and industrial-grade salt products. A mixture consisting of industrial grade magnesium hexahydrate (Yoneyama Chemical, purity 99.48%) and 7% in weight of industrial grade magnesium chloride hexahydrate (Ako Kasei, purity >98.0%) was used for investigations. Test results showed no significant differences in the values of the melting temperature and heat of fusion which means that the industrial product on the basis of the above salt can be successfully used as a heat storage material. The values of the heat of fusion and melting temperature remained practically unchanged after 1000 thermal cycles. In Japan, the cost of the industrial grade $Mg(NO_3)_2 \cdot 6H_2O$ is less than 3.0 US$/kg, while the cost of the industrial grade $MgCl_2 \cdot 6H_2O$ is less than 0.5 US$/kg. Some of thermo-physical properties of this composition are presented in Table 8.

Table 8 also presents data on the properties of sodium acetate trihydrate ($NaCH_3COO \cdot 3H_2O$) [59] which changes in volume by 9.3% during the liquid-to-solid transition. The data demonstrates that the specific heat capacity in the liquid state is 4.57 kJ/(kg °C) which is greater than that for water. Hong et al. [25] reported the results of their own measurements of the heat capacity and heat fusion of sodium acetate trihydrate and this data is also presented in Table 8.

Analysis of available data on thermo-physical properties of latent heat storage materials shows discrepancies in those values. Thus, in some cases the melting temperature and heat of fusion differ by 10% for the same materials, while for other properties this inconsistency is up to 50%. The existence of such a discrepancy in the heat of fusion cannot be explained simply by the difference in the level of material's chemical purity. Such a variation might be a result of using special, non-universal methods for the determination of the melting point, the heat fusion, the heat capacity and the heat conductivity. Practically all the above-cited data was obtained by measurements using DTA and DSC which are express methods and differ from classical thermo-physical methods. An example of the use of classical methods is the work by Inaba and Tu [49] in which they performed measurements of the thermo-physical properties of paraffin 53. These measurements have been performed over the temperature range in which the material was in both the solid and liquid states.

It should be noted that information on the dependency of the heat capacity, heat conductivity and density of materials on temperature in solid and liquid states is not fully available in the open literature. Meantime knowledge of this data would be very useful in the designing of heat storage devices.

2.3. Commercially produced PCMs and products

By 1990, only about 12 companies, mainly in the USA, were engaged in the manufacture of heat storage products. Manufactured heat storage modules in the form of polyethylene tubes and polyolefin balls used calcium chloride hexahydrate, sodium sulphate decahydrate, paraffin etc., as PCMs. Only storage devices built on the basis of $CaCl_2 \cdot 6H_2O$ had a guaranteed service period of 10 years, while for others this period was between 1 and 2 years.

At present, the main supply companies in the market of phase change heat and cold storage materials include Cristopia (France) [60], TEAP Energy (Australia) [61], Rubitherm GmbH (Germany) [62], EPS Ltd. (UK) [63–68], PCM Thermal Solutions (USA) [69], Climator (Sweden) [70] and Mitsubishi Chemical (Japan) [71]. A wide range of heat and cold storage materials is produced by EPS Ltd. [63]. Table 9 shows data on some materials which can be used only in solar applications and presented thermo-physical properties closely match numbers from data for pure salt hydrates. Table 10 presents some thermo-physical properties of materials produced by TEAP Energy for the heat storage purpose. There was no information available on the heat conductivity and density of materials, so this part of the information was compiled using [14]. Table 11 presents data on thermo-physical properties of various paraffins produced by Rubitherm GmbH which can be used in solar systems. It can be seen that the cost of these materials is relatively high which makes it difficult to use for solar energy storage. Mitsubishi Chemical Corporation has developed some prospective PCMs for heat storage but data on their properties is not published. Cristopia Energy Systems concentrates on the development of materials related to cold storage and at present it seems that only a PCM product, AC.27, can be used in solar systems. PCM Thermal Solutions currently offers the PCM manufactured by TEAP and paraffins from Honeywell. The properties of distributed paraffins are unknown. Merck (Germany) has launched its own development of PCMs [72].

Due to a phase change in the process of exploitation, PCMs are usually encapsulated in various containers. The investigations of chemical compatibility of low-temperature PCMs and design structure materials have shown that stainless steel, polypropylene, and polyolefin can be used in most cases as suitable container materials. TEAP Energy [61] uses polyolefin and polypropylene to encapsulate its PCM products. The storage materials are packed in the container in the form of spherical balls, rectangular or cylindrical bars and then are hermetically sealed. Typical plastic containers, with a diameter of 75 mm, containing the PCM are shown in Fig. 2. Each polyolefin capsule contains approximately 180 ml of the PCM. The thickness of a plastic ball is 1.2 mm. The 1-m^3 volume contains 2549 balls. EPS Ltd. [63] uses stainless-steel balls with a diameter of 100 mm. The thickness of the steel ball is 3 mm. A 1-m^3 tank holds approximately one thousand 100 mm diameter balls (Plus-ICE, 2004). Data on the heat storage capacities of the 1 m^3 of TEAP and EPS Ltd. PCM products are presented in Tables 9 and 10. The more detailed information on PCM products manufactured by EPS Ltd. is provided by Ure [64–68]. Cristopia Energy

Table 9
Thermo-physical properties of some phase change heat storage products from EPS Ltd

Trade mark	Melting point (°C)	Heat of fusion (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Heat conductivity (W/mK)	Density solid/ liquid (kg/l)	Volume expansion[a] (%)	Heat storage capacity (kJ/ball) (diameter 100 mm)	Heat storage capacity (kWh/m^3)
E21	21	150	0.68	0.43	1.48	8–9	116	32.4
E23	23	155	0.69	0.43	1.475	8–9	119	33.3
E28	28	193	2.22	0.21	0.769	8–9	101	28.2
E30	30	201	0.69	0.48	1.304	8–9	137	38.3
E32	32	186	0.78	0.51	1.460	8–9	142	39.8
A32	32	145	2.20	0.21	0.845	9–10	95	26.6
E44	44	105	1.61	0.43	1.584	8–9	87	24.3
E48	48	201	0.70	0.45	1.670	8–9	176	49.1
E50	50	104	1.59	0.43	1.601	8–9	87	24.4
E58	58	167	2.55	0.69	1.505	8–9	151	36.7
E71	71	123	1.86	0.51	1.690	8–9	109	30.4
E72	72	140	2.13	0.58	1.666	8–9	122	34.0
E83	83	152	2.31	0.62	1.600	8–9	127	35.5
E89	89	163	2.48	0.67	1.550	8–9	132	37.0
E117	117	169	2.61	0.70	1.450	8–9	128	35.8
A164	164	306			1.500	9–10	240	67.1

[a]Authors evaluation; E—materials on the bases of salt hydrates; A—materials on the basis of alkane/aliphatic solutions.

Table 10
Thermo-physical properties of some phase change heat storage products from TEAP Energy

Trade mark	Melting point (°C)	Heat of fusion (Wh/l)	Sensible heat solid/liquid (Wh/L °C)	Heat conductivity solid/liquid[a] (W/mK)	Density solid/liquid (kg/l)	Volume expansion[b] (%)	Heat storage capacity (kJ/ball) (diameter 75 mm)	Heat storage capacity (kW h/m^3)	Price of bulk product with shipping 100 kg (AUD/kg)	Price of encapsulated product with shiping 1000 balls (AUD/ball)
TH 24	24	70.2	2.7/2.2	0.8	1.6/1.5	8	≈45.5	≈32.2	10.90 + freight	
TH 29	29	79.0	0.67/0.99	1.09 (23 °C)/ 0.54 (38.7 °C)	1.71 (25 °C)/ 1.56 (32 °C)	8–9	≈51.2	≈36.2	9.10 + freight	5.95 + freight
TH 58	58	80.7	1.12/1.63		1.45/1.28	9–10	≈52.3	≈37.0	10.95 + freight	6.45 + freight
H 89	89	63.6	0.84/1.29	0.69 (110 °C)/ 0.60 (140 °C)	1.64 (25 °C)	8–9	≈41.2	≈29.2	10.00 + freight	

[a]Data from Zalba et al. [14].
[b]Our evaluation.

Table 11
Thermo-physical properties of some commercially available Rubitherm paraffins

Trade mark	Melting point (°C)	Heat of fusion[a] (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Heat conductivity (W/mK)	Density solid/liquid (kg/l)	Volume expansion (%)	Recommended operating temperature range (°C)	Heat storage capacity in the recommended temperature range (KJ/kg)	Price of PCM[b] (€/mton)
RT 6	≈8	≈140	1.8/2.4	0.2	0.86 (−15 °C)/0.77 (15 °C)	10	(−3)–+12	174	2900–3500
RT 27	≈28	≈146	1.8/2.4	0.2	0.87 (15 °C)/0.75 (70 °C)	10	19–35	179	2900–3500
RT 41	≈45	≈125	1.8/2.4	0.2	0.88 (15 °C)/0.76 (70 °C)	10	35–50	155	2900–3500
RT 42	≈43	≈150	1.8/2.4	0.2	0.88 (15 °C)/0.76 (70 °C)	10	36–51	174	2900–3500
RT 52	≈52	≈138	1.8/2.4	0.2	0.90 (15 °C)/0.76 (70 °C)	10	40–55	167	2900–3500
RT 54	≈55	≈148	1.8/2.4	0.2	0.90 (15 °C)/0.77 (70 °C)	10	46–61	179	2900–3500
RT 58	≈59	≈154	1.8/2.4	0.2	0.90 (15 °C)/0.76 (70 °C)	10	48–62	181	2900–3500
RT 65	≈64	≈154	1.8/2.4	0.2	0.91 (15 °C)/0.79 (70 °C)	10	56–71	173	2900–3500
RT 80	≈81	≈140	1.8/2.4	0.2	0.92 (15 °C) /0.77 (100 °C)	10	71–86	175	2900–3500
RT 90	≈90	≈163	1.8/2.4	0.2	0.93 (15 °C)/0.77 (100 °C)	10	82–97	194	2900–3500
RT 100	≈99	≈137	1.8/2.4	0.2	0.94 (15 °C)/0.77 (130 °C)	10	91–106	168	2900–3500
PK 80 A6	≈81	≈119	2.0	0.2	0.90 (20 °C)	8	71–86	149	6000

[a]Our calculations using presented data.
[b]All prices are ex works Hamburg/Germany.

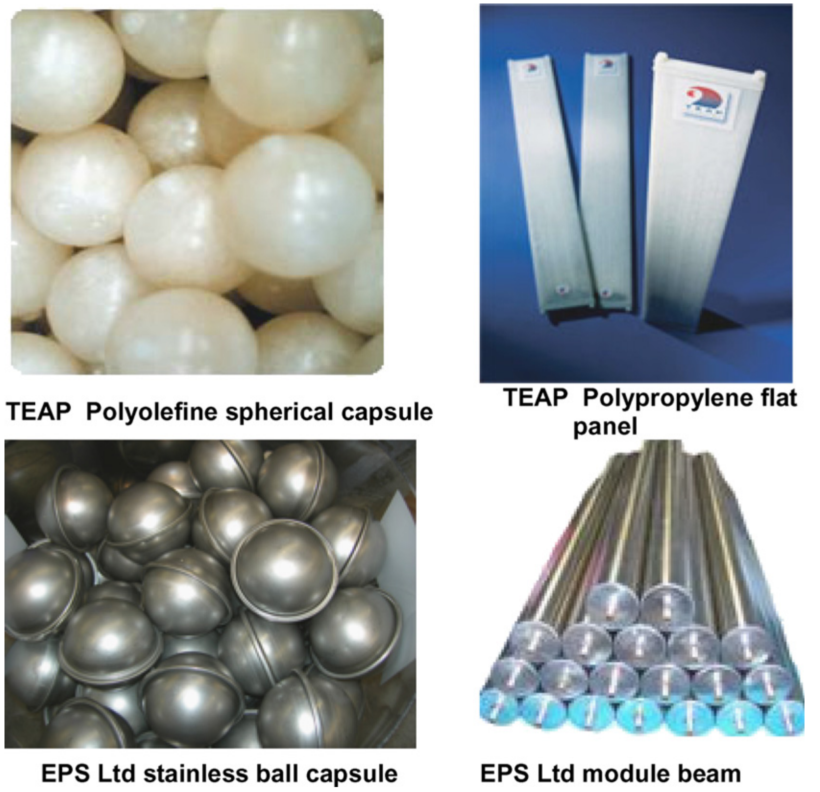


Fig. 2. Commercially manufactured phase change heat storage products.

Systems [60] seals thermal energy phase change storage materials into polyolefin balls with three diameter sizes: 77, 78 and 98 mm. This encapsulation lasts for about 10,000 thermal cycles without breaking, which is equivalent to about 20 years of operational service.

2.4. Commercially produced heat storage tanks (HSTs)

In order to use heat storage products, an appropriate heat exchange device should be designed for each particular application. However, in practice, companies produce a set of typical standardised units. Table 12 presents information on dimensions and volumes of storage tanks produced by Cristopia and EPS.

3. Methods of heat transfer enhancement

Several methods to enhance heat transfer processes in a latent heat thermal storage (LTHS) unit are used in practice and the following two are considered to be the most attractive: application of finned surfaces embedded into the heat storage medium (HSM) and an introduction of matrix structures with a high heat conductivity into HSM (or impregnation of HSM into porous matrix structure).

Table 12
Commercially manufactured phase change storage tanks

Volume (m^3)	External diameter (mm)	Total length (mm)	External surface area for insulation (m^2)	Connections inlet/outlet (mm)	Number of cradles	Empty weight (kg)	Heat transfer fluid volume (m^3)
Cristopia Energy Systems (Cristopia)							
2	950	2980	10	40	2	850	0.77
5	1250	4280	18	50	2	1250	1.94
10	1600	5240	29	80	2	1990	3.88
15	1900	5610	37	100	2	2900	5.82
20	1900	7400	47	125	3	3700	7.77
30	2200	8285	61	150	3	4700	11.64
50	2500	10,640	89	175	4	6900	19.40
70	3000	10,425	106	200	4	7300	27.16
100	3000	14,770	147	250	6	12,700	38.80
Environmental Process Systems Limited (EPS Ltd.)							
5	1250	3750		50			
10	1600	4500		80			
25	2000	8000		125			
50	2500	10,000		150			
75	3000	10,600		200			
100	3000	11,100		250			

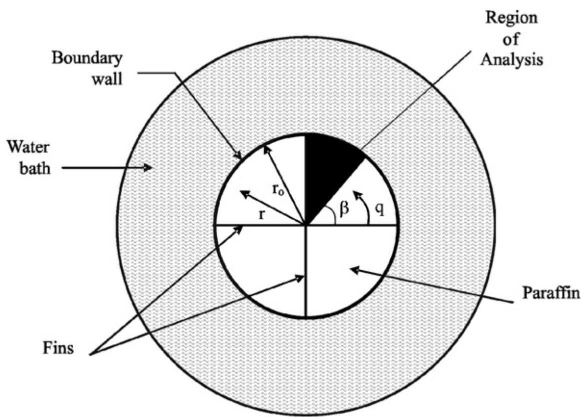


Fig. 3. A cross-section of the typical tube-fin arrangement for the LHTS system [50].

3.1. Enhancement using fin configurations

The influence of finned structures on the process of melting and solidification of PCMs was investigated in [73–84] and works by Velraj et al. [50] and Nagano [85] which are focused on the enhancement of the heat conductivity of phase change HSM. Ismail et al. [83] studied theoretically and experimentally the solidification process around a vertical tube with longitudinal fins and a heat carrier flowing inside the tube. However, the stated properties of paraffin, such as a density of 772.2 kg/m^3 both in the solid and liquid states and a heat conductivity in the liquid state of 0.089 W/(mK), contradict the data provided by Zalba et al. [14] for saturated paraffin.

Velraj et al. [50] performed an experimental analysis and numerical modelling of the solidification process of a PCM inside an internally finned vertical tube when the tube was cooled from outside, see Fig. 3. In the experiment, the storage unit consisted of a vertical cylindrical aluminium tube with outer and internal diameters of 60 and 54 mm, respectively, and length of 600 mm. Inside the tube, there were four 1.5-mm-thick fins made from the same material, 27 mm in height and 500 mm in length. The tube was filled with molten paraffin RT 60 with the melting temperature between 58 and 60 °C. This tube was placed inside another cylindrical vessel containing water. The temperature in the water bath was controlled by a thermo-stat. Initially, the paraffin and surrounding water bath temperatures were maintained at the constant level which was slightly above the solidification temperature. Then the temperature of the surrounding water bath was quickly lowered down to the value which was less than the solidification temperature and was kept at this level throughout the experiment. Numerical calculations were performed for different tube wall and fin thicknesses when the diameter of the tube was 0.06 m. Calculations show that there is no reduction in the heat transfer until the wall and fin thicknesses are reduced to the value of 1.5 mm. The experimental results demonstrated that when the number of fins exceeded four, then the fins could have different heights. Some fins could be restricted to have a height equal to a half of the tube radius. Fig. 4 demonstrates results obtained on the complete solidification time for the tube with and without fins. It can be seen that in case with the finned tube the time for a complete solidification could be approximately determined as $1/n$ of the case where there is no fins in the tube.

In [82], the same researchers investigated the variation in the effective heat conductivity of the HSU when various highly conductive structures were embedded into the HSM. The designs considered in [82] are shown in Fig. 5. Internal longitudinal fins inside a cylindrical storage tube containing paraffin were used in the first design. In the second case, the tube was filled with Lessing rings with the diameter of 1 cm. These rings are widely used in chemical reactors to increase the surface contact. The Lessing rings are made of steel and have a thin-wall hollow cylindrical structure with a partition, see Fig. 6, and occupy about 20% of the tube's volume. Experiments demonstrate that the time needed to complete the solidification is approximately one-ninth of that for the plain tube, see Fig. 7. In the third

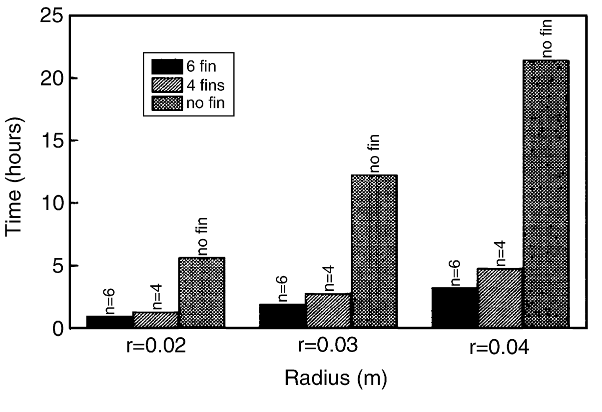


Fig. 4. Time required to complete the solidification for various paraffin tube radii and numbers of fins by Velraj et al. [50].

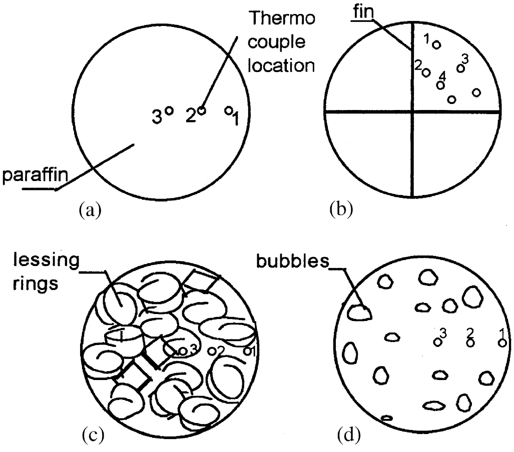


Fig. 5. Cross sections of the paraffin storage tube and locations of thermo-couples in the following configurations: (a) a plain tube, (b) a tube with fins, (c) a tube with Lessing rings, (d) a tube with bubble agitation [86].



Fig. 6. An appearance of Lessing rings [86].

design, a small amount of water is present in the tube. After adding the molten paraffin the tube is evacuated by a vacuum pump. The vacuum is maintained such that the saturation temperature of the water inside the tube is nearly equal to that of the paraffin melting temperature. The fins occupy a relatively small fraction of the tube's volume. As it can be seen in Fig. 7, the time needed to complete the solidification process in this case is approximately one-fourth of that for the plane tube. The numerical simulations show that the time factor remains nearly unchanged for the fixed number of fins irrespective of the diameter of the tube.

The effect of fins on the heat transfer ratio was also investigated by Nagano in [85]. They used water, micro-capsulated PCM slurry and salt hydrate (a mixture of 85% in weight of $Mg(NO_3)_2 \cdot 6H_2O$) + 15% in weight of $MgCl_2 \cdot 6H_2O$) as a heat storage material, see Table 13 and 14. The investigated designs of storage tubes and the scheme of the storage unit are shown in Figs. 8 and 9, respectively. The typical experimental results are also

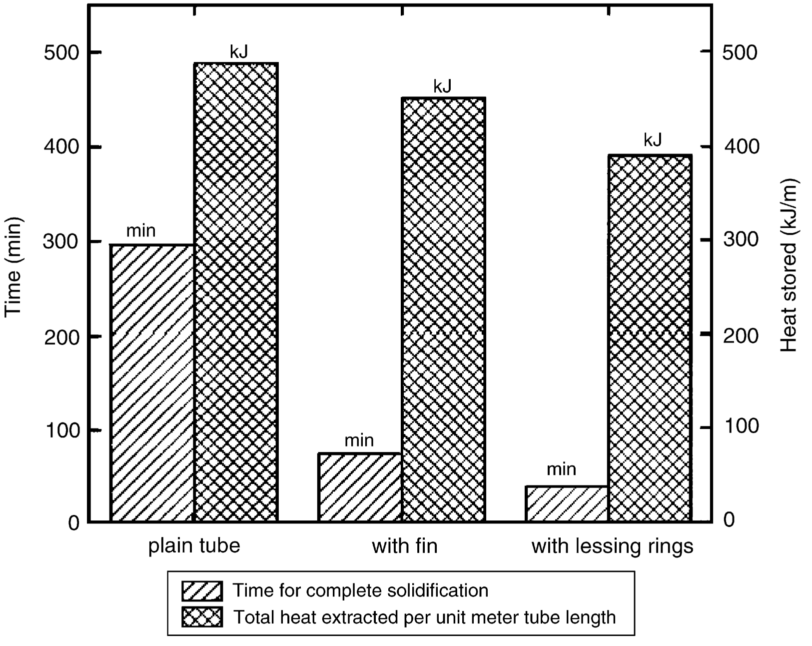


Fig. 7. The comparison of the total solidification time and the total quantity of stored heat for different configurations [86].

Table 13
Substances used for measurements [85]

Substances	(2) MCS-PCM	(3) Hydrated salts	(4) Ice-water
Melting temperature (°C)	54.3	54.3	0.4
Solidification temperature (°C)	57.9	72.2	−13.4
Heat of fusion (kJ/kg)	91.9	166	336

presented in Table 13. It can be seen that a simple increase in the number of fins does not achieve a sufficient enhancement of the effective heat conductivity. During the experiments, Nagano [85] observed a single case when the effective heat transfer coefficient was about twice the situation when a plane tube was used. The results obtained in this study contradict those obtained by Velraj et al. [50,86]. The absence of any detailed description of the experimental procedures prevents any explanation of the discrepancies.

An example of recent investigations on the enhancement of heat transfer in HSM is the paper by Stritih [87], which presents results of the experimental study of the heat transfer processes in a rectangular HSU filled with paraffin RT 30 of Rubitherm. The experimental apparatus is shown in Fig. 10. The fins for the heat transfer enhancement were made of steel with a thermal conductivity of 20 W/mK. Thirty-two 1-mm-thick rectangular fins with a height and a length of 0.5 and 0.12 m, respectively, were used. It was found that for

Table 14
Total amount of heat exchanged during a 5 h period [85]

Type of the heat exchanger	Single tube	Rectangular fins	17 Circular fins	34 Circular tubes
A heat storage material—MCS-PCM				
Type of the heat process—charging				
Total amount of heat exchanged during a 5 h period (kJ/l)	147	166	153	160
Compared to Δh (175 kJ/l)	0.84	0.95	0.87	0.91
Compared to single tube	1.00	1.14	1.04	1.09
Compared to water	1.19	1.30	1.18	1.23
Type of the heat process—discharging				
Total amount of heat exchanged during a 5 h period (kJ/l)	158	175	160	167
Compared to Δh (175 kJ/l)	0.90	1.00	0.91	0.95
Compared to single tube	1.00	1.11	1.01	1.06
Compared to water	1.24	1.30	1.19	1.24
A heat storage material—hydrated salts				
Type of the heat process—charging				
Total amount of heat exchanged during a 5 h period (kJ/l)	—	382	341	391
Compared to Δh (535 kJ/l)	—	0.71	0.64	0.73
Compared to water (210 kJ/l)	—	1.82	1.62	1.86
Type of the heat process—discharging				
Total amount of heat exchanged during a 5 h period (kJ/l)	328	392	373	418
Compared to Δh (535 kJ/l)	0.61	0.73	0.70	0.78
Compared to single tube	1.00	1.20	1.14	1.27
Compared to water (210 kJ/l)	1.56	1.87	1.78	1.99

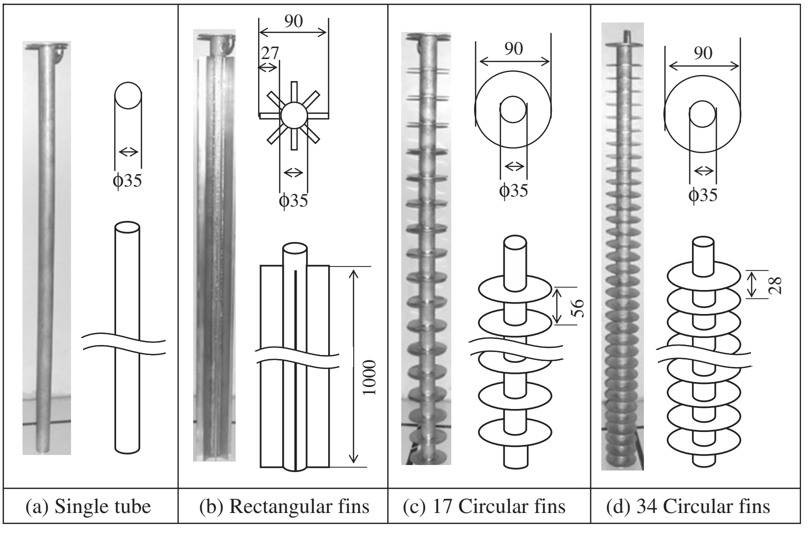


Fig. 8. The heat exchangers used by Nagano [85].

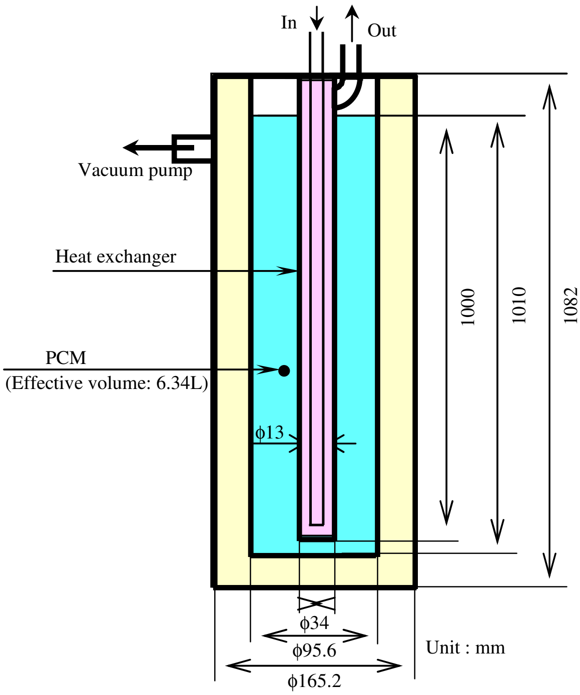


Fig. 9. A scheme of the heat exchange container [85].

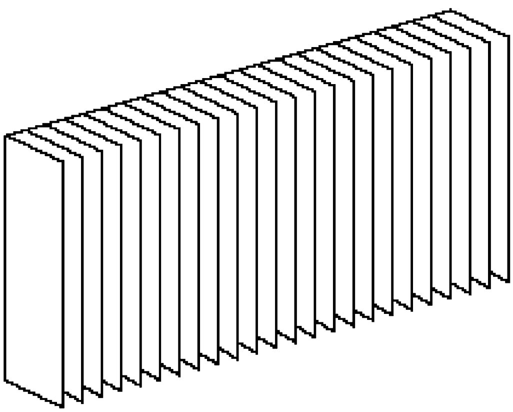


Fig. 10. Fins for heat transfer enhancement [87].

a low Fourier number, the fin effectiveness (ratio of the heat transfer with and without fins) is less than 1. The reason for this is that the natural convection, which is dominant in the process of melting, is reduced by the presence of the fins. The fin effectiveness during solidification varied from 0.5 to 3 depending on the corresponding Stefan and Fourier numbers.

3.2. Enhancement using embedded high conductive structures

In 1996, Tayeb [88] carried out the first qualitative experiment with the aim of increasing the effective thermal conductivity in such a latent HSM as a paraffin wax by embedding metallic slags and chips. Soon after, Hafner and Schwarzer [89] presented the results of the study of the effect of different metallic structures on the heat transfer in paraffin. Information on the materials investigated is shown in Table 15. Fig. 11 shows the appearance of the VSP-type aluminium filling tried in experiments. Data on measured values of the effective conductivity in the paraffin–metallic filling system are shown in Fig. 12. The VSP25 filling provided the highest thermal conductivity of 1 W/(mK), which is about six times that of pure paraffin. When studying the long-term storage performance of an experimental unit with dimensions $940 \times 845 \times 250$ mm, it was observed that the effective conductivity during the solidification process was 0.5 W/(mK), which is only half of its value at the start of the experiment. Such a reduction is due to the formation of a solid layer of paraffin along the wall of the tubular heat exchanger.

Table 15
Different materials investigated by Hafner and Schwarzer [89] as a filling in the paraffin storage system

Filling	Material	Producer	Hight of filling (mm)	Diameter (mm)	Volume fraction (%)
None	Paraffin (m.p. 55 °C)	Schümann	—	—	100
Coils	Aluminum	Lathery	—	ca. 3	ca. 5
Plastic	HDPE	Schümann	ca. 10	5	ca. 40
Lessing	Steel	Prym, Stolberg	8	8	20
Pall25	Aluminum	VFF, Ransbach	50	50	2
Pall40	Aluminum	VFF, Ransbach	25	25	2
Spirals	Stainless-steel	Spontex	—	3	—
VSP25	Aluminum	VFF, Ransbach	25	25	2
VSP50	Aluminum	VFF, Ransbach	50	50	2



Fig. 11. Aluminium fillings with VSP 25 and VSP 50 structures [89].

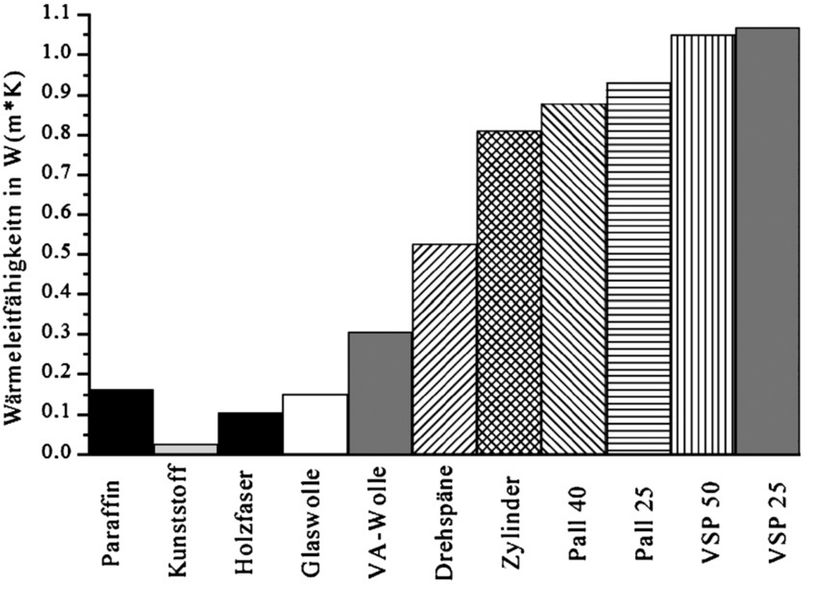


Fig. 12. The heat conductivity of different paraffin-metal filling LHSMs [89].

Table 16
The time for the melting/freezing front to progress a 1-cm distance during cooling and heating and the calculated average heat flux [90]

Storage material	Time (min)		Average power (W/m^2)	
	Heating	Cooling	Heating	Cooling
Water	55	30	1.1	2.2
Water + stainless steel	45	30	1.5	2.1
Water + copper	25	20	2.6	3.1
Water–graphite composite material	15	10	4.2	5.9

The following three methods of heat transfer enhancement in cold storage using water/ice as a PCM, were compared by Cabeza et al. [90]:

- adding stainless-steel tube pieces, which had 16 and 18 mm internal and external diameters, respectively, and 25 mm in length,
- adding copper tube pieces with the same dimensions as above,
- introducing the graphite matrix impregnation to a PCM.

The results obtained are summarised in Table 16 and it can be seen that the addition of stainless-steel tube pieces resulted in only a slight improvement, while adding the copper and graphite produced 50% and 150% improvement in cooling, respectively.

In 1996, Satzger and Eska [91,92] from the Bavarian Centre for Applied Energy Research (ZAE Bayern) proposed a method to store thermal energy in a composite material consisting of a PCM embedded in a matrix of expanded graphite (MEG). Similar



Fig. 13. A slice of the PCM–graphite composite material [95].

composite materials were investigated also by Mehling [93] and Mehling et al. [94]. A slice of the MEG produced by SGL Carbon GmbH (Germany) is shown in Fig. 13. The typical volume fractions in the PCM–graphite composition were 10% in volume of graphite, 75–85% in volume of a PCM, with the remaining volume filled with air. Depending on the volume fraction of the graphite in the composition, the effective thermal conductivity was increased from 0.2 W/(mK) for pure PCM to 25–30 W/(mK). This increase is greater by factor of 10 than that achieved by using metallic rings and it is up two orders of magnitude in comparison with pure PCM. Instead of an increase by a factor of 3, the heat flux in LHTS with similar composite materials was increased by a factor of about 10. At the same time, the heat storage density went down by only about 20%.

Requirements also were analysed which had to be satisfied by LHTS units with a PCM in order to use them for space and hot water heating. The authors investigated a storage unit which consisted of four independent storage modules with RT 50 paraffin and MEG. The total storage volume was 224 l, the melting temperature was 54 °C and the heat of fusion was equal to 146 kJ/l. The performance of the HSU was investigated in conditions which were very close to that of the real application. The main conclusion from this study was that a new HSU could be integrated into the residential heating system and satisfy the peak demand for heat. The PCM–graphite composition based on the paraffin had a storage density that was about three times greater than that of water. The use of the new salt hydrate material developed by Merck KGaA would make it possible to increase this by factor of 4.

Xiao et al. [95] have developed a shape-stabilised thermal storage material on the basis of the mixture of a technical-grade paraffin (with the melting point of 56–58 °C) and a styrene–butadiene–styrene (SBS) tri-block co-polymer. To improve its thermal conductivity, this composite consisted of paraffin, SBS and exfoliated graphite (EG) with a weight parts ratio of 80:20:3. A typical curve for the solidification process of this paraffin–SBS–EG composite is presented in Fig. 14 and the time for the completion of the solidification process is two-ninths of that for pure paraffin.

The carbon fibres are considered as a prospective material that might be used to enhance the heat conductivity in the heat storage systems with PCMs. There are various carbon fibres available commercially with a thermal conductivity close to that of aluminium and

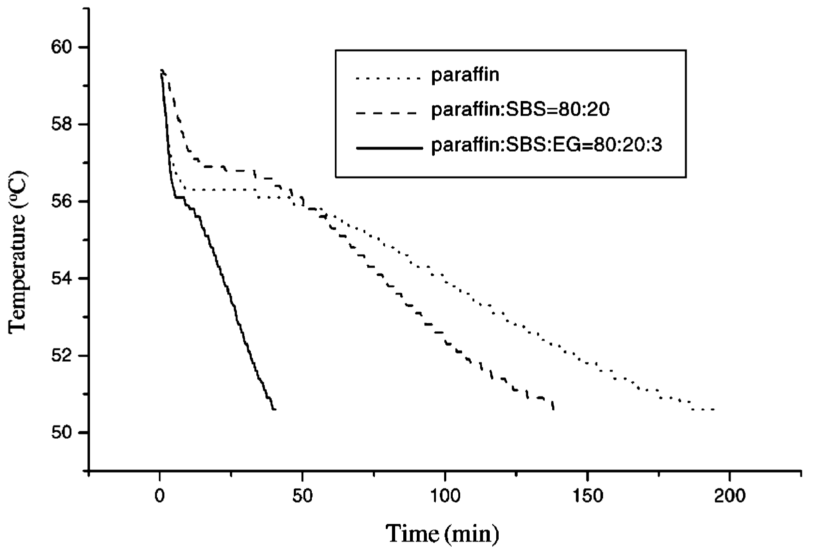


Fig. 14. The cooling process of pure paraffin and composite PCMs, $T_{ini} = 59.5\,°C$, $T_{bath} = 50\,°C$ [95].

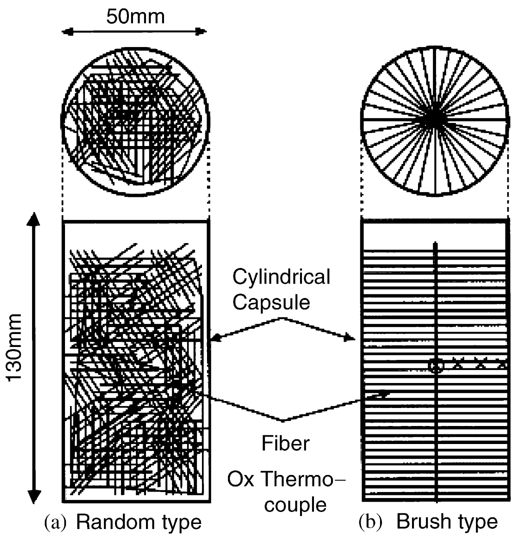


Fig. 15. Using carbon fibres inside a cylindrical capsule [96].

copper. According to Fukai et al. [96], the thermal conductivity of some products is greater than 1000 W/(mK). The authors studied two heat transfer enhancement techniques using carbon fibres. In the first case, the fibres were randomly distributed in a PCM. In the second experiment, carbon fibres were oriented along the direction of the heat flow. For investigations, the carbon fibres with the diameter of 10 μm, density of 2170 kg/m^3 and thermal conductivity of 220 W/(mK) at the room temperature conditions were used.

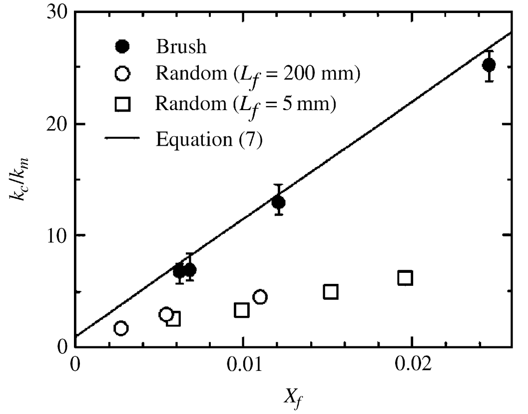


Fig. 16. The enhancement of the thermal conductivity in a phase change material [96].

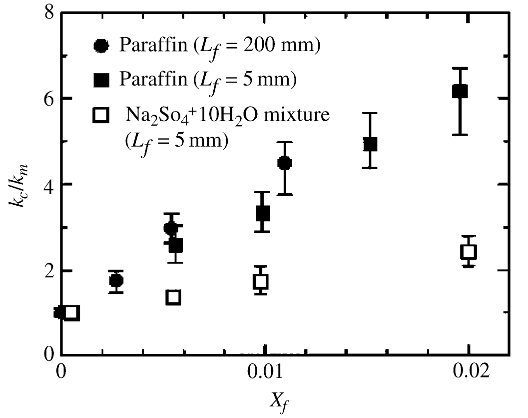


Fig. 17. The enhancement of the thermal conductivity in phase change materials using random carbon fibres [96].

The phase change temperature and the thermal conductivity of the paraffin wax used in experiments at the solid state were 41–43 °C and 0.26 W/(mK), respectively. The fibres with the paraffin wax were placed into a cylindrical steel capsule with the diameter of 50 mm and height of 130 mm. In the first series of experiments, the carbon fibres with the lengths of 5 and 200 mm were randomly placed in the capsule, see Fig. 15(a). In the second case, a brush made of carbon fibres was inserted into the capsule as shown in Fig. 15(b). In both cases, after placing carbon fibres, the capsule was filled with molten paraffin. Figs. 16 and 17 illustrate some results obtained in [96]. As it can be seen, the effective thermal conductivity increased by a factor of 6 when 2% of the randomly packed carbon fibres were used in the composite material. The increase factor was about 25 for the case when 2.5% of the composite material was made by the carbon fibre brush. Experiments demonstrated that even a small fraction of carbon fibres added to a PCM could significantly enhance the heat transfer in energy storage systems.

Fukai et al. [97,98] presented results of further experimental and numerical investigations of thermal characteristics of a carbon fibre brush/PCM composition used

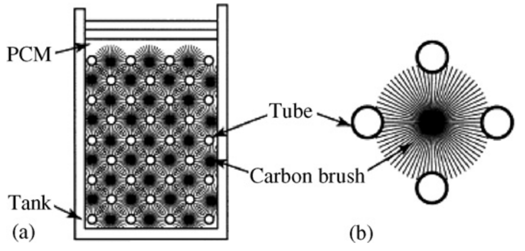


Fig. 18. A thermal energy storage unit filled with brushes made of carbon fibres [97].

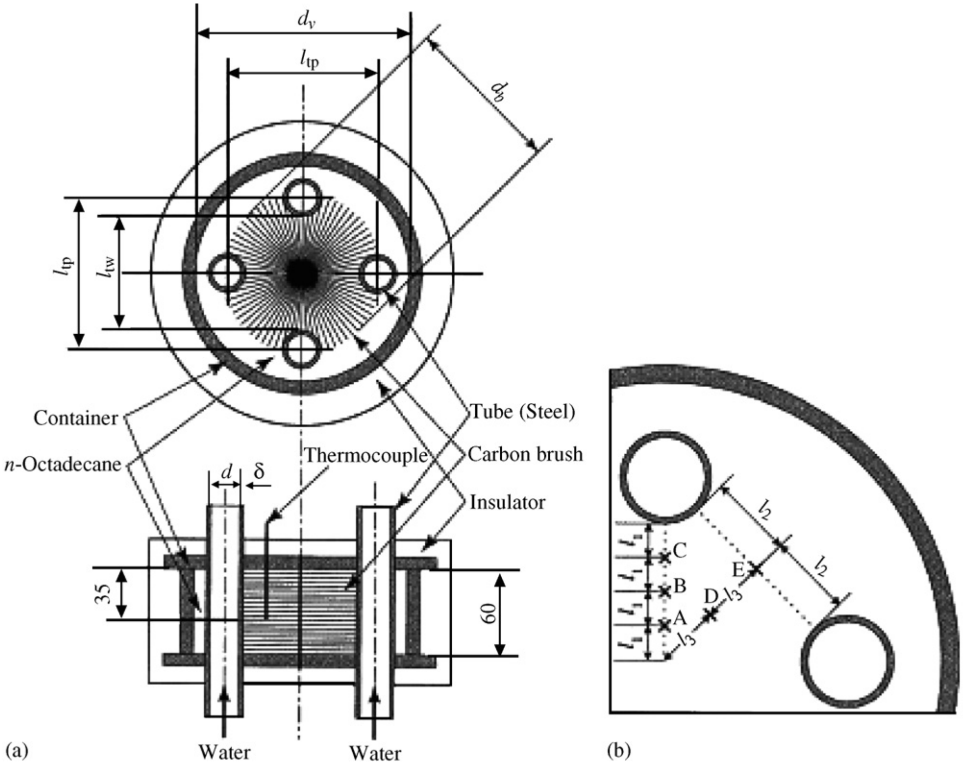


Fig. 19. A scheme of an experimental apparatus and the location of thermo-couples [97].

in a shell-and-tube-type thermal energy storage system. The experimental apparatus used in this study is shown in Figs. 18 and 19. In the experiments, in which *n*-octadecane was used as a PCM it was found that the effective thermal conductivity of the composition, taking into account the effect of the thermal resistance, was about three times greater than that of a PCM when the volume ratio of fibres is 0.012. The thermal conductivity of the composition, taking into account the thermal contact resistance between the fibres and the tube surfaces, was estimated by Fukai et al. [98] to be 0.40 and 0.51 W/(mK) in the solid state for the cases when the volume ratio of fibres was 0.004 and 0.008, respectively.

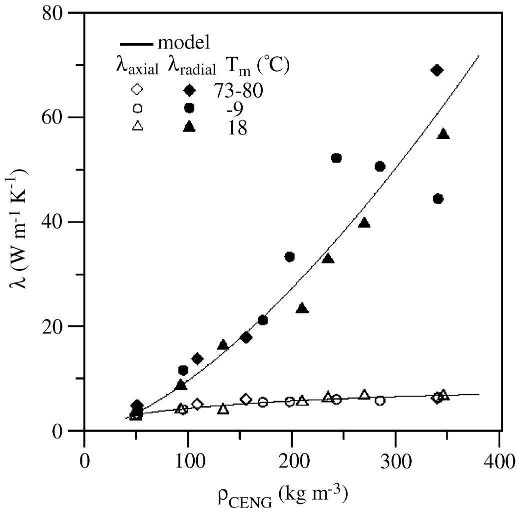


Fig. 20. The axial and radial thermal conductivity as a function of the bulk graphite matrix density for paraffin/CENG and raw CENG [99].

Py et al. [99] investigated a new phase change composite material made of paraffin and the compressed, the expanded, natural graphite (CENG) matrix. The effective conductivity of this composite material, consisting of 65–95% of paraffin by weight was experimentally measured and calculated, and the results are presented in Fig. 20. The variation in this value reflects the different amounts of graphite in the composition (since it is defined by the anisotropy of graphite).

Thus, the recent achievements in the development of new heat storage materials on the basis of traditional PCMs and advanced graphite structures provide new opportunities for the heat transfer enhancement in thermal storage systems if a reliable contact between the composite material and the heat exchange surface can be achieved.

4. Passive solar heating systems with latent heat storage structures

Zalba et al. [14] analysed the use of various structural components for thermal storage purposes. More detailed information on energy conservation in buildings can be found in Khudhair and Farid [100]. In the last two decades, a significant contribution to the development of latent heat storage materials and heat storage systems has been made by scientists at the Centre for Building Studies, Concordia University (Canada). Results obtained were presented by Athienitis et al. [101], Banu et al. [102,103], Feldman et al. [38,39,40,104,105,106,107], Hawes et al. [108,109], Lee et al. [47], Scalat et al. [110] and Shapiro et al. [111]. The Centre carried out investigations using numerous organic materials. First, pure substances were tested and then organic materials of the commercial grade were studied. The thermo-physical properties of some of the materials, obtained as a result of these investigations, were also considered earlier in this paper.

As a result of long-term tests on organic materials, Feldman et al. [40] found that mixtures of commercial esters, such as methyl palmitate (65–95%) and methyl stearate (5–35%) were suitable for cooling applications. These mixtures have a melting interval of

22–25.5 °C, a freezing interval of 24.5–22.5 °C and an effective latent heat of about 120 kJ/kg. A mixture of butyl stearate (BS) (49%) and butyl palmitate (48%) has a melting temperature interval of 17–21 °C and a latent heat of melting of 138–141 kJ/kg, therefore it was recommended by the Centre for Building Studies as a suitable composition for the storage of the thermal energy in buildings. An additional advantage of this composition is its relatively low cost. The composition was incorporated into gypsum wallboards using a technology, developed by Feldman et al. [38,108], with its weight making up about 20–25% of the total wall's weight. A comparison of conventional wallboards and those with PCMs showed that:

- A PCM wallboard provided an eleven fold increase in the energy storing capacity (with a 4 °C temperature rise),
- The difference in the thermal conductivity was within the range of $\pm 15\%$, depending on the PCM,
- The flexural strength and durability were comparable after freeze-thaw cycling,
- While the flame velocity was slightly greater in PCM wallboards, their fire resistance, in general, was excellent,
- Full compatibility with fasteners, paints and wall-papers.

Rudd [112] carried out similar investigations of a 0.5 inches thick gypsum wallboard impregnated with a coconut fatty acid 625. It was found that after 5 min of submersion into molten coconut oil at a temperature of 40 °C the weight of the wallboard increased by 25%. A PCM's weight fraction of 25% in total weight of the saturated wallboard was chosen for further tests since after exceeding this concentration a dripping of the oil was observed. These results were in good agreement with those obtained in the Centre for Building Studies by Shapiro et al. [111] and Feldman et al. [38–40] for other organic compositions. The typical amount of PCM in the wallboards was 2.14 kg/m^2 of the wallboard and the cost of the PCM used was 1.72 US$/kg. Two identical side-by-side test rooms with dimensions $3.35 \times 3.35 \times 2.44$ m were used for a full-scale PCM wallboard evaluation. It was found that the thermal storage of the room with the PCM wallboards was 2.1 greater than that of the room with conventional wallboards when the temperature was increased from 18.3 to 29.4 °C. The useful heat storage was limited by the low value of the heat transfer coefficient between the air and the wallboards. Another significant problem reported by Feldman and Banu [39] was the presence of an unpleasant odour in the room with the PCM wallboards. Tests performed on samples demonstrated that the odour could be almost completely eliminated if the PCM wallboards were kept at the temperature of 93 °C for several hours. A further problem reported by Rudd [112] was that a layer of corrosion formed on some metallic (copper and aluminium) surfaces in the room with PCM due to the vapourisation of impurities from the fatty acids. It was believed that this problem could be resolved by the evaporation of the volatile impurities in the fatty acids before it was used to treat the wallboards. Finally, it was found that without the addition of fire retardants organic PCMs had unacceptable flammability characteristics.

Athienitis et al. [101] presented the results of investigations of the thermal performance of a passive solar test-room with a wall latent heat storage system. In these investigations, an existing outdoor test-room was used with dimensions $282 \times 222 \times 224$ cm. Gypsum boards with a PCM were placed over the existing gypsum boards on the vertical walls of the test room. The total area of the PCM vertical wallboards was approximately 20 m^2 and

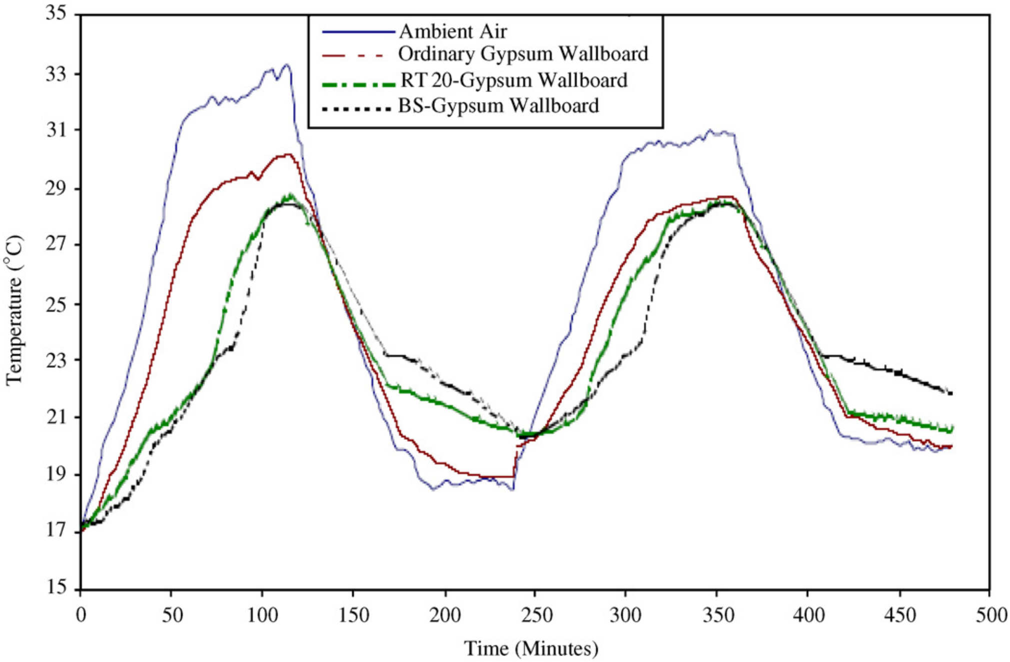


Fig. 21. The thermal behaviour of a PCM wallboard during heating–cooling cycles [113].

the total mass of the PCM used was 47 kg. BS was used as the PCM with a phase change interval of 16–20.8 °C. The PCM gypsum board contained about 25% by weight of BS. The experiments were conducted under winter weather conditions with outside temperatures as low as −25 °C. During the tests, the room temperature was set to 23 °C during the daytime (from 6:00 a.m. to 5:00 p.m.) and to 16 °C for the rest of the time. When the room air temperature changed, the PCM in the gypsum board underwent the solid–liquid transition in the phase change interval of BS (16–20.8 °C). When the temperature exceeded 20.8 °C, then the PCM wallboard acted as a latent heat storage device and when the temperature dropped below 16 °C, then energy was released back into the living space. These full-scale experiments demonstrated that the application of PCM–gypsum boards in a passive solar building can bring down the maximum room temperature by about 4 °C during the day, thus preventing overheating, and during the evening and night (7–11 h in total) the surface temperature of the PCM gypsum board was approximately 3.2 °C higher than the surface temperature of the conventional wallboard so that heat was returned to the room.

Khudhair et al. [113] also investigated the thermal performance of a gypsum wallboard with a PCM. In these experiments, they used wallboards which had been submersed in the molten PCM for several minutes. Two wallboard samples with dimensions $100 \times 100 \times 10$ mm were impregnated with paraffin (23.2% in weight of RT20) and BS (22% in weight of BS) and its thermal performance was compared with that of a control wallboard without a PCM. Thermal cycling was carried out by forcing warm and cold air over the same side of the board and typical curves for thermal cycling tests are presented in

Table 17
The calculated heat storage values for various PCM-block combinations (Lee et al. [47])

The type of the block	A	A	A	R	R
PCM	BS	P	P	P	P
% PCM in block	5.6	8.4	8.4	3.9	3.9
Temperature range (°C)	15–25	22–60	45–60	22–60	45–60
Storable sensible heat in blocks (kJ)	1428	5337	2107	7451	2941
Storable sensible heat in PCM (kJ)	233	1136	449	705	278
Storable latent heat in PCM (kJ)	977	2771	2082	1718	1291
Total storable heat (kJ)	2638	9244	4638	9874	4510
Total storable heat/storable sensible heat in block	1.9	1.7	2.2	1.3	1.5

Fig. 21. For clarity, only one set out of many measurements was used in the discussion. Warm and cool air with the temperatures of 30–33 and 17–20 °C, respectively, was used for the heating–cooling cycles, thus, the PCM was completely melted and frozen. Thermal cycling tests for the above two PCMs demonstrated that there was no tendency for the PCM to migrate within the wallboard and there was no sensible deterioration in the thermal energy storage capacity of the wallboard.

Earlier we discussed results from investigations of the behaviour of PCMs in gypsum wallboards installed inside buildings. However, the application of PCMs outside building structures has an equal significance, since this is also an effective way of storing solar energy on clear days and preventing buildings from overheating during the warm part of the year. Lee et al. [47] investigated the heat storage capability of a concrete block containing a PCM. In this study, the thermal storage performance of ordinary concrete blocks and those containing two different PCMs were investigated. One PCM used was commercial BS, Emerset 2326, and the other commercial paraffin (P), Unicere 55. Common concrete blocks of dimensions $20 \times 20 \times 40$ cm with a hollow core were used in the experiments. Two types of these blocks, namely R (regular) and A (autoclaved), were tested and the results compared. Impregnation of the concrete blocks with a PCM was achieved by immersing each block in a bath filled with a constant volume of liquid PCM kept at a constant temperature. The blocks were heated to the appropriate temperature and then immersed until the required amount of the PCM was absorbed. The blocks tested in experiments had the following average PCM loading % in weight:

- 5.6% for the A-type block impregnated with BS (ABS),
- 8.6% for the A-type block impregnated with paraffin (AP),
- 3.9% for the R-type block impregnated with paraffin (RP).

Table 17 presents the calculated heat storage values for the corresponding concrete blocks.

It can be seen that the presence of a PCM in sufficient volume doubled the heat storage capacity of the block.

Manz et al. [114] reported results of experiments with an external two-layer passive wall system made of a transparent insulation material (TIM) and a translucent salt hydrate. A honeycomb was a combination of a salt hydrate PCM and a TIM, see Fig. 22. The PCM was placed in commercially available glass blocks and part of the incident solar radiation

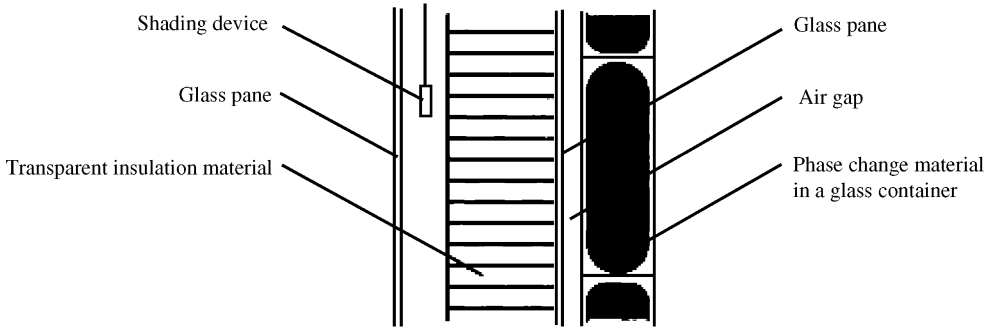


Fig. 22. A prototype of a TIM–PCM external wall system for solar space heating and day-lighting [114].

was used for lighting. At low temperatures, the PCM was in a solid crystalline state and because of scattering by the PCM the light transmitted to the room was diffused. The melting process was induced by the absorption of part of the incident radiation in the storage medium itself. The stored solar energy then could be used for space heating purposes. The heat is transported to the room from the inner surface of the storage block by both free convection and infrared radiation with the transparent insulation cover reducing the heat losses from the storage device to the environment. In order to prevent overheating in summer, a roller blind with a high solar reflectance on the outer surface was attached to the wall. At night, the roller blind could be shut so that heat losses in the heating season were reduced. Commercially available calcium chloride hexahydrate with additives making up to 5% of the total mass was used as the PCM. The authors concluded that the effect of the use of this phase change energy storage (PCES) system was positive. A disadvantage of the chosen PCM was the backscattering of the solar radiation from the solid-state PCM leading to the reductions in the heat and light gains.

5. Active solar heating systems with latent heat storage structures

One of the first attempts to use a PCM for solar heating was undertaken by Telkes and Raymond [115] in Dover (USA). The single-storey private house consisted of five rooms, including two bedrooms. The house was 135 m^2 in floor area, 23 m long and one room deep. The solar energy was accumulated using 18 solar collectors made of thin gauge galvanised absorber plates, black painted and covered by double 1.2×3.0 m glazing panels. The heat generated from these panels was passed through a duct via a fan to three heat storage bins situated on either side of the rooms. The heat storage bins contained five gallon drums filled with sodium sulphate decahydrate (Glauber's salt). With a total of 21 tons of this PCM, the system had the potential heat storage capacity of 11 GJ, sufficient to store energy equal to 12 days of heating load, when used between the room temperature and 32 °C temperature (melting point). The house was completed in 1948 at a cost of $20,000, with the cost of the solar heating appliance equal to $3000. The system operated successfully for 2 years, providing a comfortable temperature of 21 °C with no secondary back-up heating system required. However, the experiment ended in failure due to the decomposition of the salt. At that time, the method to eliminate this problem with the PCM was undeveloped.

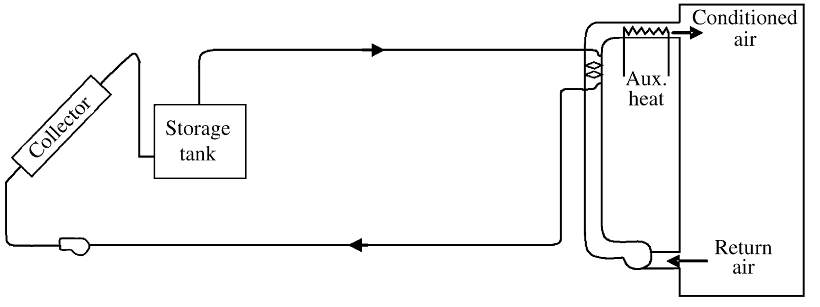


Fig. 23. A schematic diagram of the basic solar energy system in Trabzon [119].

Table 18
Some parameters of the water-based system in Trabzon (Kaygusuz [119])

Collector		System circuit pipe	
Number of glass covers	1	Length	40 m
Thickness of glass cover	4 mm	Diameter	40 mm
Refractive index	1.45	Heat losses	20 kJ(hK)
Collector plate absorptance	0.90	Fluid density	1000 kg/m^3
Collector emmitance	0.85	Fluid specific heat	4.197 kJ/kg K
Collector efficiency factor	0.85	Ambient temperature	18 °C
Back and side losses	1.20 kJ/h m^2 K	Energy storage tank	
Mass flow rate	40 kg/h m^2	Volume	3.65
Total collector area	30 m^2	Thermal losses	0.210 W/m^2 K
Number of collector	18	Shape (L/D)	2.46
		Ambient temperature	18 °C

Another project using PCM heat storage technology was realised by the Canadian scientists J.W. Hodgins and T.W. Hoffman [6]. The two-storey residential house comprising 111 m^2 of floor area was completed in 1957 and used 12 tons of the nucleating Glauber's salt, thickened with sodium silicate and containing chromate corrosion inhibitor. As in the earlier design, the PCM was contained in vertically arranged steel cans, yet again this experiment ended unsuccessfully due to the degradation of the PCM.

The experience gained in the above two failed attempts prompted Jurinak and Abdel-Khalik [116–118] to numerically model air and liquid-based solar heating systems using PCMs as the HSM. The influence of the storage capacity magnitude, the storage unit heat transfer characteristics, the collector area and the location on the system performance were investigated using sodium sulphate decahydrate and paraffin wax.

The next example of experimental and theoretical investigations of latent heat storage for a water solar heating system is work performed by Kaygusuz [119]. The system investigated is shown in Fig. 23 and the parameters of the system are presented in Table 18. As it can be seen in Fig. 23, the system was designed to heat a laboratory building, see Table 19, and consisted of a solar collector, an energy storage tank, a water-to-air heat exchanger, an auxiliary electrical heater, a water circulating pump and measuring and

Table 19
Construction properties of the laboratory building in Trabzon (Kaygusuz [119])

Window area (single glass, $U = 4.8\,W/m^2\,°C$-day)	$75\,m^2$
Wall area (single brick, $U = 1.6\,W/m^2\,°C$-day)	$60\,m^2$
Floor area (concrete, $U = 2.5\,W/m^2\,°C$-day)	$75\,m^2$
Ceiling area (concrete + flat metal, $U = 2.0\,W/m^2\,°C$-day)	$75\,m^2$
Effective UA (kWh/°C day)	0.800
Comfort temperature	22 °C
Average degree days for heating season (°C-day)	2500
Average total heating loading in heating season (kWh)	19,500

Table 20
Climatic conditions in Trabzon over a heating season period (Kaygusuz [119])

Average outdoor temperature	9.35 °C
Minimum outdoor temperature (February)	−3.40 °C
Average minimum outdoor temperature	2.30 °C
Maximum outdoor temperature (May)	29.10 °C
Average maximum outdoor temperature	22.91 °C
Average relative humidity	74.85%
Average wind velocity	2.5 m/s
Average solar insolation	$5.10\,MJ/m^2$ day

control equipment. Table 20 summarises data on the climatic conditions in Trabzon, Turkey for 1991. The collected solar energy was transferred to the storage tank which contained polyvinyl chloride tubes with 1500 kg of calcium chloride hexahydrate. Whenever the space heating load was required, it was satisfied using the energy storage tank and the auxiliary energy source. During the heating season, the measured values of the mean collector and storage efficiencies were 0.60 and 0.70, respectively, with the 30-m^2 water solar collector used in the system. The solar-supplied fraction in the load was not as high as the collector and storage efficiencies for the same collector with the PCM, and its maximum value was around 0.30–0.35 because there were several days with cloudy conditions in the Trabzon region during the tests. A simulation programme based on the models of Morrison and Abdel-Khalik [118] was used to perform a theoretical study of the solar heating system with the PCES. The results obtained from these studies are presented in Fig. 24. As it can be seen, the solar fraction rose substantially when the specific storage mass was increased to 25–30 kg of $CaCl_2 \cdot 6H_2O/m^2$ of the solar collector. Although the further increase in the specific storage mass did not provide sufficient gains in the solar fraction. The author concluded that PCES using calcium chloride hexahydrate or sodium sulphate decahydrate could be effectively used for thermal energy storage, especially in a solar-assisted heat pump system for domestic heating (Table 21).

Esen and Ayhan [125] reported results of a numerical simulation of a short-term heat storage system based on a storage tank with a PCM. These results demonstrated that the PCM properties, the cylinder radius, the mass flow rate and the inlet temperature of a heat transfer fluid (HTF) must be very carefully chosen in order to optimise the performance of the storage tank. Two years later Esen et al. [126] considered theoretically two different cases to describe the transient behaviour of the phase change unit. In the first case, tanks were considered in which the PCM was packed in cylinders and HTF flowed parallel to

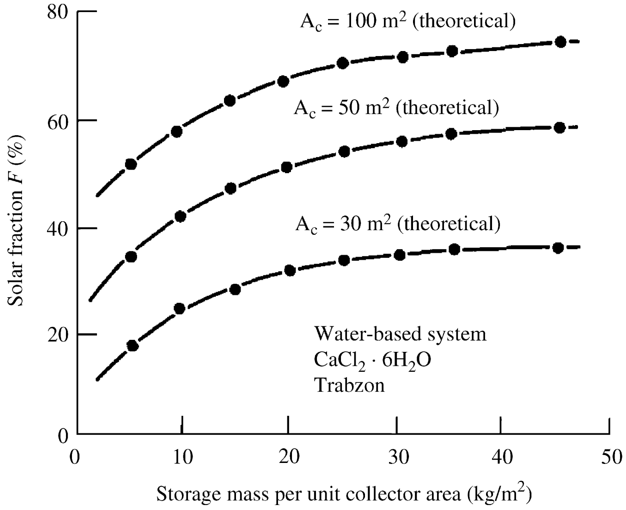


Fig. 24. The variation of the solar-supplied fraction of the thermal load in the system with storage mass and collectors for water-based systems with PCES in Trabzon [119].

Table 21
Main characteristics of solar greenhouses with latent heat storage

Reference	Used phase change material	Total amount of PCM (kg)	Green-house size (m^2)	Specific amount of PCM per m^2 of ground area	Total area of solar air collectors	Solar fraction (%)
Kern and Aldrich [120]	Calcium chloride hexahydrate	1598	36	44.4	17.2 m^2	38–43
Takakura and Nishina [121]	Calcium chloride hexahydrate	300	7.2	41.6	1.6 m^2	
Jaffrin and Cadier [122], Jaffrin et al. [123]	Calcium chloride hexahydrate	13,500	500	27		
Levav and Zamir [124]	Calcium chloride hexahydrate	3000	200	15		
Takakura and Nishina [121]	Sodium sulphate decahydrate	2500	25	10		
Kürklü et al. [144]	Sodium sulphate decahydrate	192	13.5	14.2		29–30
Nishina et al. [136]	Polyethylene glycol	200	7.2	27.8	1.6	

these cylinders (mode 1). In the second case, HTF flowed through the pipes surrounded by the PCM (mode 2). The results of the modelling demonstrated that the thermo-physical properties of the PCM determined its melting time and that the selection of the PCM and configuration of the store should be considered simultaneously. It was also found that to store more of the incident solar energy, mode 2 was preferable. Finally, Esen [127] investigated experimentally and theoretically heat transfer processes in the cylindrical phase change storage tank coupled with a solar powered heat pump system. The same

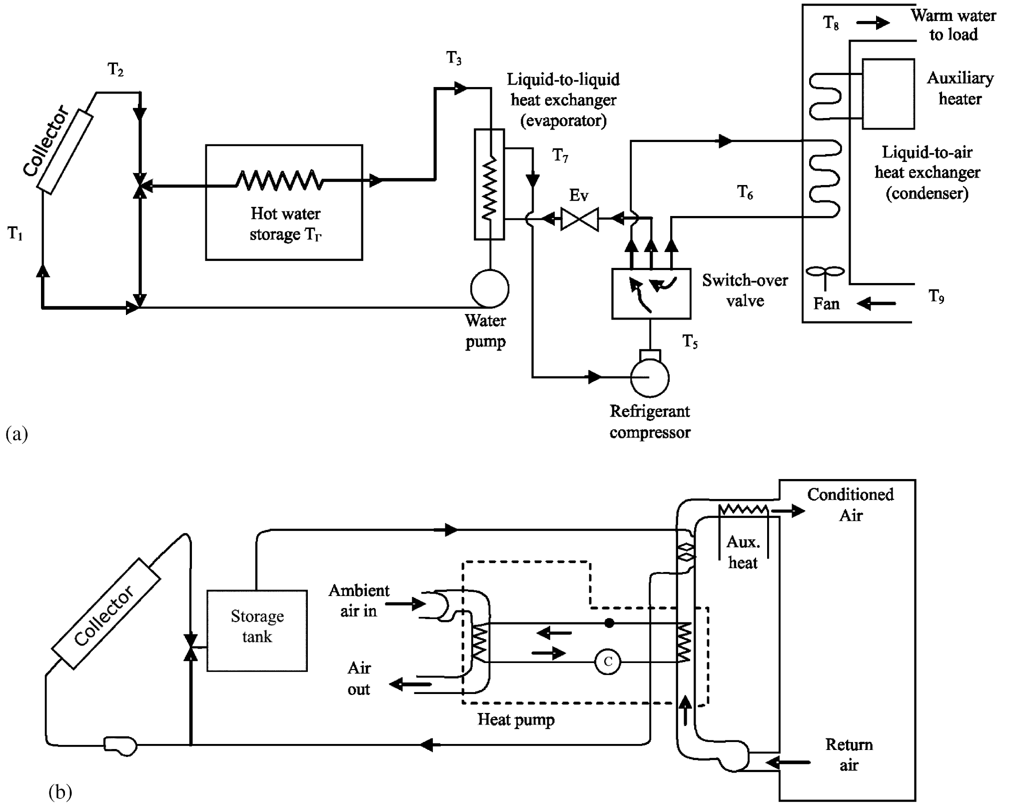


Fig. 25. Solar-assisted heat pump systems: (a) connected in series and (b) parallel connection [131].

equipment was used by Çomaklı et al. [128–130] and Kaygusuz [119] in experiments in which a 4.25-m^3 latent HST was filled with 1090 kg of encapsulated calcium chloride hexahydrate. Water solar collectors were installed facing the equator at the angle of 48° from the horizontal surface. The main conclusion drawn from studying the above system was that the heat stored and then extracted by the heat pump from the storage tank was insufficient for heating purposes.

Kaygusuz [131–133] also investigated both experimentally and theoretically a solar-heat pump system using latent heat storage for residential heating. This heating system, including the heat pumps, is shown in Fig. 25. Two sources of heat were used in the experimental setup. Two operational modes of the system were studied, namely (a) when the heat pump system was connected to the storage tank in series, (b) the heat pump system was connected to the storage tank in parallel. The experimental results demonstrated that relatively high 60–68% collector efficiency could be achieved using 30 m^2 flat-plate water heating collectors in the operational mode (a), while the collector efficiency varied from 48% to 60% in the operational mode (b). However, the energy storage efficiency was less than that for collectors. The average net storage efficiency of 62% was registered for both operational modes. The average seasonal heating performance values were 4.0 and 2.5 for

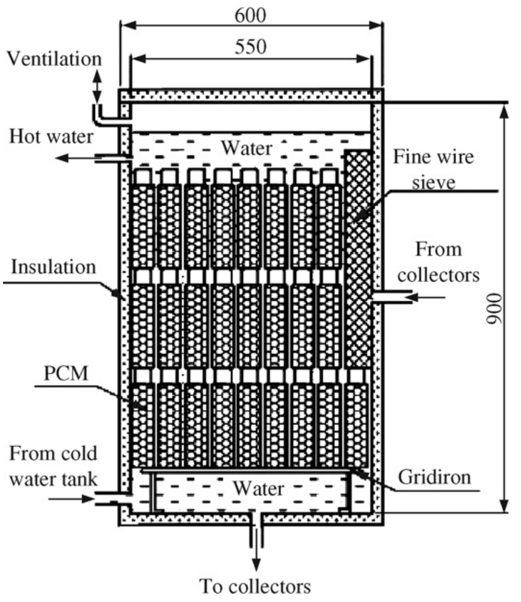


Fig. 26. A cross-section of the cylindrical heat storage tank with a PCM [134].

(a) and (b) modes, respectively. The following conclusions were made as the result of the above investigations:

- the parallel heat pump system saved more energy than the series heat pump system. The reason was that the parallel system used both air and solar as a heat source for the evaporator, while the series system used only the solar heat stored in the tank;
- the application of only the solar system was not sufficient to provide heating for the laboratory building for the given climatic conditions with considerable amount of cloudy days;
- substantial energy savings could be achieved by using a heat pump system with combined solar and waste energy heat sources;
- polyvinyl chloride was used to make the container in the above work and its conductivity was too low. Therefore, the solar energy collected during the day was not sufficient to melt the entire PCM in the storage. As result, the amount of the experimentally stored energy was lower of that used in theoretical calculations;
- calcium chloride decahydrate was preferable as a PCM in the given region.

Recently Canbazoğlu et al. [134] presented some results of investigations on solar energy storage performance using sodium thiosulfate pentahydrate in a conventional solar water heating system. In this study, authors used an experimental, open-loop conventional passive solar energy system with a natural circulation to provide domestic hot water. The system consisted of solar collectors, hot and cold water tanks and was equipped with sensors to take measurements.

Fig. 26 shows a cross-sectional view of the well-insulated cylindrical galvanised steel HST with a 190-l volume and incorporating a PCM. Here, 0.44 l polyethylene bottles containing 0.735 kg of the thiosulfate pentahydrate were placed in the tank in three rows. The volume of the PCM and water in the HST were 107.8 and 82.2 l, respectively, with the total mass of the PCM being 180 kg. The total heat accumulated in the HST with the PCM was approximately 2.6–3.5 times greater than that of the conventional solar energy system having the HST without the PCM. The extra cost of the solar thermal energy storage system including the PCM was estimated to be US$ 0.5/l of the HST volume.

6. Application of PCMs in heating solar greenhouses

The application of PCMs in greenhouses to store solar energy was initiated in the 1980s. Thus, Kern and Aldrich [120], Nishina and Takakura [121,135], Nishina et al. [136], Jaffrin and Cadier [122], Jaffrin et al. [123], Boulard et al. [137], Machida et al. [138], Baille and Boulard [139], Levav and Zamir [124] and Kürklü et al. [140–144] carried out extensive investigations on the application of PCMs for greenhouse heating. The analysis of data from the above investigations was performed by Kürklü [144] and presented in Table 17. Calcium chloride hexahydrate, Glauber's salt (sodium sulphate decahydrate) and polyethylene glycol were used as a PCM. All the storage systems of solar greenhouses accumulated solar energy in the daytime and used it for heating at nights or during cloudy periods. The researchers from Çukurova Unıversıty ın Adana (Turkey) [145–149] also designed and built a seasonal heat storage system for greenhouse heating. This system consisted of solar air heaters, a seasonal HSU, a plastic greenhouse and a computerised data aquisition/control unit. The external heat collection unit (HCU) consisted of 27 m^2 of south-facing solar air heaters. On average, there were 0.15 m^2 of the absorber surface per square metre of the greenhouse ground surface. A cylindrical tank with the diameter of 1.5 m and the volume of 10 m^3 was used as the seasonal HSU. Two coils made from a corrugated PVC tube with a total length of 97 m and a diameter of 10 cm were used as the heat exchanger installed in the HSU. The HSU's volume per square metre of the greenhouse ground surface was 0.055 m^3 and the HSU's volume per square metre of the solar air heaters was 0.37 m^3. The HSU was filled with 6000 kg of paraffin which is an equivalent of 33.3 kg of paraffin per square metre of the greenhouse ground surface. The melting temperature interval and the latent heat of fusion of the PCM were 48–60 °C and 190 kJ/kg, respectively. The experimental greenhouse of floor area 180 m^2 (15 m × 12 m) and gutter height 2.3 m was made as a galvanised steel pipe structure covered with a single layer of PE film. Unfortunately, no data on the performance of this storage system was published.

7. PCMs in solar cooking systems

Solar cookers are thought to have great potential in countries with a hot climate and they were the subject of intensive investigations [52–55,150–172]. The application of solar cookers is restricted if they are not equipped with a heat storage system since it is impossible to use them in cloudy conditions or evenings.

It appears that Domanski et al. [166] were the first to experimentally investigate the possibility of cooking during off-sunshine hours using PCMs. In their investigation, they used a non-conventional design of a box-type solar cooker with multi-step inner reflectors,

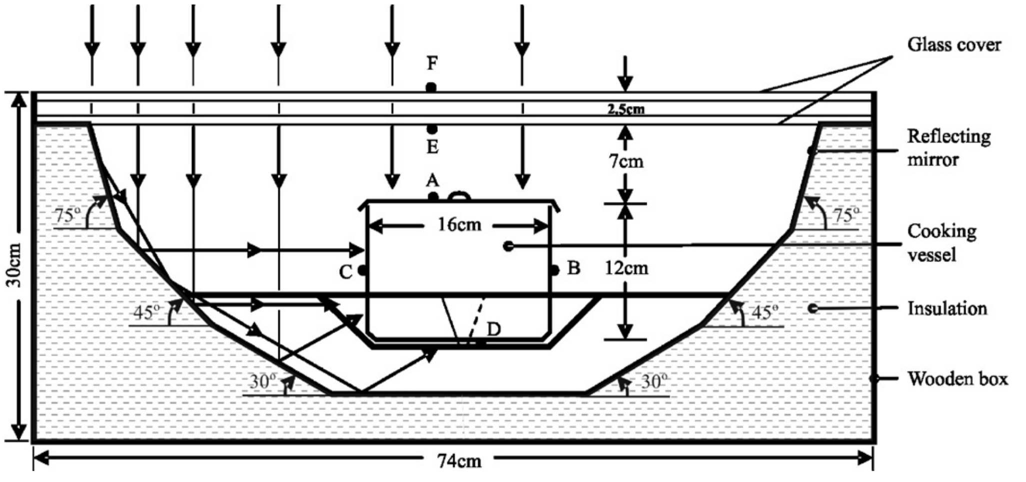


Fig. 27. A schematic diagram of the solar cooker by Domanski et al. [166].

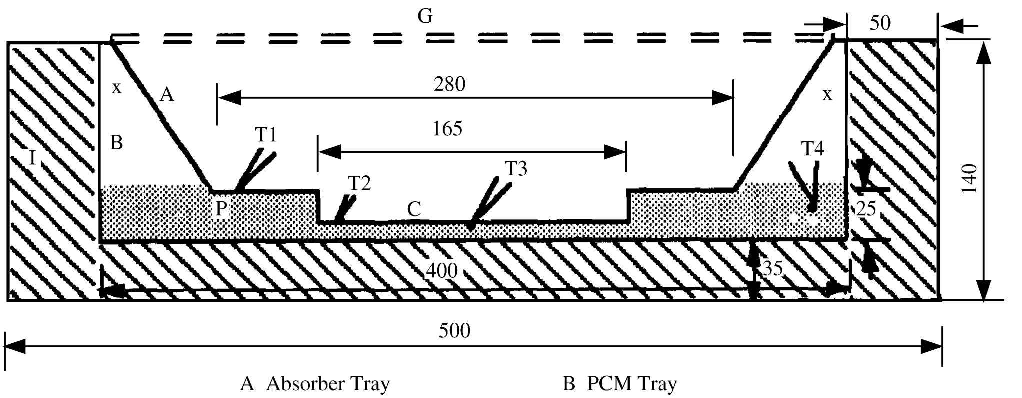


Fig. 28. A schematic diagram of the solar cooker box with a heat storage [167].

see Fig. 27. The storage-cooking unit consisted of two aluminium concentric cylindrical vessels with the 1.5-mm-thick walls, which were connected together at their tops using four screws to form a double-wall vessel with a gap between the outer and inner walls. The outer vessel had a diameter of 180 mm and height of 120 mm, while the inner vessel had a diameter of 140 mm and height of 100 mm. The annular gap between the outer and inner vessels was 20 mm. The outside surface of the outer vessel and covers were painted using a conventional black paint. The gap between the outer and inner vessels was filled with 1.1 kg of 95% commercial stearic acid, or 2 kg of magnesium nitrate hexahydrate,

produced by Aldrich Co. It was established that the heat discharging time tends to increase with increasing the initial temperature of the cooking medium and the degree of superheating of the liquid PCM, but it decreased as the mass of the cooking medium increased. The resulting values of the overall utilisation efficiency of the cooker were about 3–4 times greater than those for steam and heat-pipe solar cookers which could be used for indoor cooking. The cooker under investigation could achieve higher temperatures by using PCMs when the melting point exceeds 100 °C (for instance, magnesium chloride hexahydrate has the melting temperature of 116.7 °C).

Buddhi and Sahoo [167] also proposed to use a PCM in solar cookers. The commercial stearic acid with the melting point of 55.1 °C and the heat of fusion of 160 kJ/kg was used as a latent heat storage material. A similar cooker (see Fig. 28) in the form of the aluminium cooking pot, which is 0.16 m in diameter and 0.06 m in height with the lid, is widely used in India to cook rice. The solar cooker contained about 3.2 kg of stearic acid and although experiments indicated that this design allowed users some time to cook when there was no sunshine, the amount of the stored heat was inadequate and the melting temperature of the PCM was not sufficiently high. In 2000, Sharma et al. [52] reported that they had developed a much-improved design of solar cooker using a latent heat storage material. As a PCM, they tested the commercially available acetamide with the melting point of 82 °C and the heat of fusion of 263 kJ/kg. Experiments demonstrated that such a cylindrical latent HSU with a cooking pot was capable of storing energy which then was used in the evenings. To make this possible, the melting point of the PCM must be between 105 and 110 °C. Experience gained demonstrated that solar cookers without concentrating systems or high quality solar collectors could have a very limited application. Therefore, to increase the performance of a box-type solar cooker, Buddhi et al. [53] suggested using three plane adjustable reflectors. This technique made it possible to use as a latent heat storage material a commercial grade of acetanilide with a melting temperature of 118.9 °C and a heat of fusion of 222 kJ/kg. Even then, the technical performance of the box-type solar cookers was quite poor, since it was possible to cook only 0.3–0.4 kg of rice over a 2-h period. Therefore, in order to improve the performance of solar cookers, it has been suggested that they were coupled with evacuated tube solar collectors (Balzar et al. [152] and Kumar et al. [159]) and concentrating systems (Mullick et al. [160], Habeebullah et al. [156] and Öztürk [168]).

Schwarzer and de Silva [169] tested a collector with reflectors using pebbles as the thermal storage for cooking purposes. Sharma and Sagara [170] and Sagara et al. [171,172] tried out evacuated tube solar collectors to develop a solar cooker with a latent heat storage. Thus, they used two vacuum-tube collector units having a net absorbing area of 1.82 m^2 each (Nippon Electric Glass Co., Japan) and erythritol as a latent heat storage material with the melting point of 122 °C and the heat of fusion of 338.8 kJ/kg. The storage unit had two hollow concentric aluminium cylinders, and its inner and outer diameters were 304 and 441 mm, respectively, and it was filled with 45 kg erythritol, which was used as a PCM. The cooking vessel itself was 297 mm in diameter and 300 mm in height and could be easily placed inside the PCM storage unit. Cooking experiments demonstrated that the developed HSU was able to store an adequate amount of heat to cook in the day and the evening. This type of solar cookers with a latent heat storage system is quite expensive but it has a good potential for community applications. At present further research is in progress on new PCMs which could be used effectively in solar cooking applications.

8. Conclusions

The above analysis of data published in the open literature allows us to draw the following conclusions.

1. Practically, all the experiments on the properties of prospective PCMs were restricted to measurements of the melting temperature and the heat of fusion. The main methods used by researchers in studying the thermal properties of PCMs were ''quick'' methods such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC). It is a well-known fact that the results obtained with the use of these methods can considerably differ from those obtained using rigorous thermo-physical methods. The significant discrepancies in the data published on the properties of PCMs demonstrate that the accuracy of the above express methods is not sufficiently high. The review also shows that, except in a very few cases, no measurements were performed to establish the temperature dependence of the heat conductivity, the heat capacity and the density of prospective PCMs. For the creation of high-performance solar applications, it is of paramount importance to have accurate information on the temperature dependency of the properties of prospective PCMs. Additionally, it is of critical significance to study thermo-physical properties of some pure substances with melting temperature in the range between 0–150 °C, which then can be used as a reference material or standards by all interested parties for the calibration of their experimental devices and equipment.
2. It appears that there are no national or international standards developed and implemented to test thermal energy storage products and there is no single national or international scientific centre to certify PCMs and the latent heat storage products produced and distributed by manufacturers. Producers, as a rule, do not have quality certificates and it is very difficult or impossible to obtain exact data on thermo-physical properties of PCMs. The development of unified international standards to test thermal energy phase change heat storage products would assist to improve the situation.
3. None of the heat storage products which are commercially available on the market have heat transfer enhancement capabilities which would improve performance of low-temperature devices. At present, this is mainly an area of interest for academic researchers. The means for enhancement of heat transfer in heat storage devices with a PCM are the use of fins and Lessing rings from various materials and carbon fibres.
4. Prospective applications of PCMs include heating of buildings by placing them in the walls of houses and solar greenhouses in regions with sharp continental climate, namely countries with a very hot summers and very cold winters.
5. At present, the cost of PCMs is quite high. For example, paraffin products of Rubitherm GmbH cost 2900–3500 €/ton and the price for a salt hydrate product is 9000–11,000 Australian dollars/ton. At these prices, application of PCMs is mainly restricted to research or demonstration projects. For large-scale solar energy applications, the cost of latent heat storage products should be on the level of 1 US$/kg. This aim can be reached only if technical grade materials produced with a minimum of technological processing are used. Hence, research on solar applications of PCMs should include investigations of such low-grade materials.
6. When developing commercial latent heat storage products at acceptable prices, stability of thermal properties of these substances should be tested for at least 1000 thermal

cycles. For example, Sarı and Kaygusuz [24] reported substantial changes after 910 thermal cycles in the thermo-physical properties of even such stable organic substances as fatty acids.

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